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PAPERS ACCEPTED FOR PUBLICATION:

Ammonium Phosphomolybdate and the Reducing Action of Zinc in the Reduction. By Andrew A. Blair and J. Edward Whitfield.

An Improved Gas Regulator. By F. P. Dunnington.

A Modification of Hinman's Explosive Pipette. By Augustus H. Gill.

The Ferrates. By Claude A. O. Rosell.

Inspection of Cotton for use in the Manufacture of Guncotton. By Charles E. Munroe.

The Periodides. By Albert B. Prescott.

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Proceedings.

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MEETINGS OF THE SECTIONS.

CHICAGO SECTION.

At a meeting held June 3, in the chemical lecture room at the Northwestern University, School of Pharmacy, the Chicago Section of the American Chemical Society was organized with the following officers: Frank Julian, President; J. C. Foye, Vice-President; F. B. Dains, Secretary; J. H. Long, Treasurer. Executive Committee, Frank Julian, A. L. Smith, and F. B. Dains.

The Section then adjourned until the regular meeting in September.

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THE CHEMICAL HISTORY OF A CASE OF COMBINED ANTIMONIAL AND ARSENICAL POISONING.[1]

BY CHARLES A. DOREMUS, M.D., PH.D.

Received May 17, 1895.

THE coffin plate disclosed on opening the outer box of rough wood, bore the inscription, "Gustave H. M. J. Baum, died March 30th, 1892. Aged 26 years, 3 months, and 4 days." It was untarnished and affixed to a black cloth-covered casket. The condition, not only of the outer and that of the inner case, but also that of the lining of the latter and of the clothes about the body excluded the possibility of there having been any infiltration of liquid from the grave and rendered the examination of any soil from the cemetery superfluous.

The emaciated body of a medium sized man was identified by the physician who had attended him in life and verified his death and by the undertaker and his assistant who had prepared the body for burial.

Though three months had elapsed since the interment, it was possible on July 6th, 1892, to recognize the features, also an abrasion on the right shin. There was some mould about the face and body, the latter being disclosed when the clothing was removed. The features of the corpse bore a marked resemblance to a photograph of a man named Ludwig Brandt.

Both Baum and Brandt had been quondam acquaintances of a Dr. Henry Meyer. Insurance had been secured on the life of

[1] Read at the May Meeting of the New York Section.

Baum in four companies, amounting in all to $8,500. Brandt had personated Baum in making application for these policies, had come to New York in company with Dr. Meyer, a woman posing sometimes as Mrs. Meyer, at other times as Mrs. Baum, and one Mueller.

After the death of Brandt the woman applied to the different insurance companies for the sums due, representing herself as his widow. Several of the companies paid in full, a total of $4,000.

Accompanied by Dr. Meyer she visited the offices of the Mutual Life Insurance Co., of New York. The interview aroused suspicions which were subsequently increased by the sudden disappearance from New York of the parties, their effects having been sold and no word being left of their destination.

At the instigation of Mr. Daniel Gillette, of the Mutual Life Insurance Company, detectives were sent in search of the parties with the view of unearthing any crime that might have been committed. Mr. H. G. Julian, acting in this capacity, had been able to secure a description of the supposed Baum, and found the body to agree not with him but with a photograph and description of Brandt.

Dr. L. W. Schultze, one of the coroners of the city, deemed this initial evidence of sufficient weight to order an autopsy and conducted it with his medical assistants. Dr. S. P. Minden, who identified the body, had attended the man for three weeks before his death, and gave a death certificate ascribing the demise to chronic dysentery. He had not noticed any unusual circumstances during this attendance. Had not Dr. Meyer borne an unenviable reputation, it is probable that no further notice would have been taken of the case; but because of his career extra caution was taken at the autopsy to determine, if possible, if the pathological condition agreed with the diagnosis of the physician.

The surface of the body was carefully scrutinized. There were no marks of hypodermic injections, however, nor any evidence of embalming by arterial or other injections. The undertaker declared that no attempt was made to embalm the body and that no embalming fluid was used upon it or injected into

it. Three channels for the introduction of poison; *viz.*, imbibition from the soil, the use of embalming liquids, and the use of hypodermics were thus eliminated. Coroner's physician, Dr. O'Hare, and Prof. D. Hunter McAlpin, who at a subsequent time examined the viscera with Dr. O'Hare, could find no gross or microscropic pathological evidence of importance, so that full light as to the cause of death was not obtainable from the autopsy. At the autopsy Dr. S. P. Minden related the symptoms he noticed during his attendance on the patient. They did not develop any theory of death other than dysentery, but left the case still obscure. Later he kindly furnished copies of the prescriptions he had written. At the trial, testimony was given to show that some of these prescriptions had been filled but there was no evidence that the medicines had been administered. However, since remedies such as morphine, opium, copper arsenite, and bismuth subnitrate had been prescribed, it became necessary to consider them in any scheme of chemical analysis. The advisability of a chemical analysis was discussed and decided on as necessary to fully determine the cause of death. There was every probability that great skill had been used in the administration of any toxic agent or that some unusual poison had been employed.

Though due care was exercised at the autopsy to detect the odor of any volatile poison none was perceptible and there were no circumstances that in any way directed attention to that class of poisons. The analysis proper, therefore, was begun with the treatment of portions of the viscera for the alkaloids. For this purpose the stomach and its contents, one half of the intestine and its contents, and one-half of the liver, and some fluid which had exuded from it into the abdominal cavity at the time of the autopsy, were treated.

Freshly rectified alcohol was placed on each separate part, 500, 600, and 800 cc. being used respectively. The organs were comminuted and the alcohol acidulated with tartaric acid. The jars remained in an ice chest until a thorough maceration was effected. The alcohol and washings with alcohol was filtered from the tissue and the undissolved substances, which latter were utilized for the detection of inorganic poisons, as were also such other

residues from the extraction as could be utilized for this purpose.

The necessity for doing this is not generally recognized. Some of the salts of the metallic poisons are quite soluble in the menstrua employed in extracting the alkaloids and pass into solution with the latter. Previous cases had shown this, one which the writer examined as associate expert, involving the detection of morphine in an embalmed body, very markedly.[1]

In this latter instance, it was of paramount importance that the arsenic extracted in large quantities from the viscera should be separated from the trace of morphine that might coexist, and a prolonged series of extractions was resorted to to eliminate the possibility of mistaking the reactions of the one for the other. This procedure was also necessary to anticipate what was subsequently brought forward by the defence, *viz.*, a point raised by Otto.[2]

The production of arsines and other metallo-organic compounds must also not be lost sight of, for both in testing for organic and inorganic poisons, these exceptionally interesting compounds have been and are likely to be important objects of toxicological research. The fact that evidence of metallic poisons is obtainable from the extractions practised to separate the alkaloids must always be borne in mind, no matter whether the Stas, Erdmann-Uslar or Dragendorff method is employed, or some modification of them, as also when dialysis is resorted to.

Such a course is especially necessary in cases where, in order to recover the very minute quantity of alkaloid that may still remain in a stomach or intestine, the whole of either organ and its contents is submitted to processes for its recovery. Failure to detect an alkaloid may with these precautions in some cases be followed by the finding of an inorganic poison.

It is doubtful whether the method prescribed in many foreign countries, and followed in the laboratory of toxicology in Paris,[3] of comminuting each organ and then mixing together weighed portions of each and of submitting the composite mass to analysis is altogether a wise or safe proceeding. Our own experience is much against it.

[1] People vs. Robt. W. Buchanan, 1600.
[2] Otto: Ausmittelung der Gifte, *1884*, 117.
[3] Documents du Laboratoire de Toxicologie, Paris, *1891*, 23.

The chances of detecting any alkaloid are greatly reduced and the same can be said of metallic poisons. The unequal distribution of poisons through the viscera, and the retention of poisons in certain organs in preference to others, are two of many reasons why a mixture of a fourth of several, say, stomach, intestine, liver, brain, and kidneys, is inadvisable. Nor can there be any hard and fast rule laid down to apply to all cases in the search of poisons. The judgment of the expert must determine in some measure the method to be pursued, and he will naturally have in mind the facts which have been ascertained heretofore, and which have led to the establishment of rules of procedure.[1] No matter what course is followed, it will sometimes happen that important data in regard to the distribution or absorption of the poison detected are unobtainable which could have been secured had the nature of the poison been manifested in the symptoms or indicated by the history of the case. Where, therefore, prominent symptoms are developed, or the autopsy reveals the character of the poison, even if only to so slight an extent as to indicate whether organic or inorganic, narcotic or corrosive, it may best subserve the ends of justice to examine the contents of the stomach apart from the tissue, the gall-bladder and its contents separately from the liver. The fluids of the intestinal tract and the compacted fæces near the rectum separately from each other and the tissue. Much will depend in adopting a course as elaborate as this upon the time that has elapsed since death. A long interment would obliterate to a great degree the clearness of the picture of the distribution of the poison in the body, which we might expect to have developed.

While recent analytical results have tended to show that poisons rapidly diffuse in the body, either when injected post-mortem or imbibed by application to the skin, or though taken in life have afterwards permeated the tissues and reached other organs, we take issue with the claim advanced by the defense in this trial, that toxicology is utterly unable to-day to decide whether a poison extracted from the body has or has not been administered before death.

Though weighable quantities of copper were obtained from the

[1] Dragendorff Ermittelung von Giften, 4, *1884*.

liver and brain in the case now before us, only traces were found in other organs and in some none at all. Such facts are inexplicable on the basis of post-mortem diffusion. It is therefore of great moment to determine more closely not only the localization of a poison but how intimately it is combined with the tissue. A simple permeation may have taken place, or a definite union or fixation, and such union would often be indicative of vital processes. The employment of suitable solvents will thus lead us to a diagnosis between such true chemical compounds and mere loose impregnations. Tissues are found by the dyer to absorb only certain dyes though they may be transiently stained with others. When in contact with poisons, certain living tissues "dye in the wool."

The alcoholic extracts of stomach, intestines, and liver, were evaporated each by itself and each residue thus obtained treated with strong alcohol and filtered. The new alcoholic extracts now of small volume were again evaporated and their aqueous solutions while still acid treated successively with petroleum ether, benzene, and amyl alcohol. All of these liquids had been especially rectified. After the last amyl alcohol extraction was effected several fresh shakings with petroleum ether were resorted to to remove amyl alcohol from the watery liquid. The aqueous solution was then made alkaline by ammonium hydroxide, and the extractions with petroleum ether and benzene conducted as before. The solution was then acidified, hot amyl alcohol added and emulsified, then enough ammonium hydroxide added to render the solution alkaline. This procedure was repeated often enough to make sure of the extraction of any morphin. Six residues were thus obtained from each of the three viscera. It was a noticeable feature of this case compared to two other investigations made just previously that the residues were of less quantity than in either of the other cases, and that many were indeed so insignificant as to be incapable of purification. Residues I, II and IV were very slight or inappreciable.

Of course, residues VI, from the alkaline liquid extracted by amyl alcohol were submitted to the closest scrutiny. Not only had morphin been prescribed, but it was desirable to ascertain if the ptomaines present might either give or mask the morphin

reactions. After suitable purification they were tested. The morphin reactions were not obtainable, some of the ptomain reactions were pronounced. Minute quantities of morphin solution added to portions of the residues could be detected by appropriate tests. The physiological test of morphin applied to a frog was not obtained. Neither morphin nor other poisonous alkaloid could be identified in any of the residues.

The inorganic poisons claimed attention next. Small quantities of copper arsenite had been prescribed; bismuth also as subnitrate. These metals might therefore be present.

The comminuted tissues, subsequently residues from parts treated for organic poisons, were disintegrated by hydrochloric acid and potassium chlorate. Fresenius and von Babo's method was applied to the stomach first and the results obtained showed the necessity of using the same process with the other organs. A copious precipitate formed the moment hydrogen sulphide was conducted into the faintly acid liquid which had been previously deprived of chlorine by bubbling carbon dioxide through it. The color of the precipitates thus obtained varied with the different organs, but was evidently metallic and not of organic nature. The precaution was taken in the analysis of each separate organ to subject the liquid after saturating it with hydrogen sulphide to warmth and long standing to effect a complete precipitation of the metals.

The precipitates were collected, redissolved in small quantities of hydrochloric acid and potassium chlorate and reprecipitated with previous precautions.

The purified sulphides were washed free of chlorides by dilute hydrogen sulphide water and a separation of the different metals attempted.

It will shorten the story considerably to state that mercury, lead, bismuth, and tin were not detectable in any organ. That zinc was tested for carefully in the filtrate from the hydrogen sulphide and not found.

That antimony and arsenic and in some organs these and copper were separated and identified.

Ammonium sulphide was found to dissolve the washed precipitate entirely or to leave only a small amount of copper sul-

phide. This solution was evaporated and oxidized by nitric acid. Then fused with sodium carbonate and sodium nitrate. When copper was present a dark mass separated. In other cases a white powder was suspended in a clear liquid and all became a white solid on cooling.

At this juncture one of the greatest obstacles was met.

Otto[1] would have us believe that the separation of antimony from arsenic by Meyer's method is as facile and as complete as the destruction of organic matter. He enters into a discussion concerning the methods of manipulation and gives a device for still further preventing dissolved antimony from producing a mirror in the Marsh test by conducting the gases evolved over caustic alkali, a very objectionable process as we shall see later, and comes to the conclusion that the method is reliable.

Notwithstanding all this, the history of this analysis shows first, that when very small quantities of antimony are present they would escape notice when the fused mass is dissolved in water and possesses an *alkaline* reaction as required; secondly, that where much antimony is present it is advisable to resubject the insoluble residue to a second fusion to remove possible traces of arsenic.

The finding of antimony and arsenic in the first organ analyzed, naturally put us on our guard in the testing of others.

Where much antimony was found, there was of course an insoluble white residue, but the brain and muscle contained so little that only the most painstaking work enabled us to detect the antimony and separate it from the arsenic. Since some antimony remains in the Marsh apparatus, the whole not passing out as hydrogen antimonide undiscovered pyroantimoniate may go into solution when the fused mass is dissolved in water and either produce a mirror with arsenic or remain in the generator.[2]

The fact that all the antimony is not converted into gas in the Marsh process renders the use of Hofmann's silver nitrate method unserviceable for the quantitative separation and estimation of antimony and arsenic in toxicological analysis.

While all things considered Meyer's method seems the best

[1] Otto, op. cit., 164.

[2] Dragendorff Ermittellung der Giften, Dritte Auflage, 406, *1888*.

available, the experiences of this case justify us in cautioning against a too implicit reliance upon it.

The finding of antimony in the stomach was followed by detecting arsenic also. The other organs also revealed the presence of each.

In three viscera, copper was noticeable. The liver yielded 0.0056 gram, the brain and muscle, traces.

The entire quantity of copper extracted from the liver was converted by a small portion of the arsenic obtained from the same organ into copper arsenite and presented as an exhibit along with other portions of the arsenic, there being a great excess of the latter. The absence of copper from the stomach and intestines and its disproportion to the arsenic in the liver and the quantity of each poison found seemed sufficient proof to decide in the negative the question of the copper arsenite prescribed being the source of the arsenic found. Since the copper when found had passed together with antimony and arsenic into the ammonium sulphide solution, then to the fusion, it remained undissolved with the pyroantimoniate and had to be separated from the antimony. This operation followed the incineration of the filters and their contents of sodium pyroantimoniate, in either very small crucibles or porcelain dishes and the fusion of the residues with potassium cyanide. In the case of the intestine the filter was not very small since a considerable amount of sodium pyroantimoniate had been separated. The contents of the filter were removed to a capsule and the filter incinerated. A slight amount of char was left. A drop or two of nitric acid was put on this and heat applied to expel all acid. Whether this was not effectual or some trace of sodium nitrate remained undecomposed is uncertain, but sufficient was left to cause a sharp explosion when the fusion with potassium cyanide was quite well under way, projecting most of the unfused mass out of the dish. While the presence of antimony in large quantity in the intestinal tract was still clearly demonstrated from the residue left in the dish, a quantitative determination of the whole was out of the question. Otto alludes to the possibility of such an explosion in connection with Fresenius and von Babo's method of obtaining arsenic by reduction with potassium cyan-

ide and sodium carbonate, and very naively says "Mir ist bei sorgfaeltigem Arbeiten nie Derartiges vorgekommen."

Although great care was exercised, the accident did happen in the above instance and though the filter ash of the antimonial precipitates from other viscera were in one or two cases similarly treated without the slightest trouble, we caution against the use of nitric acid or an insufficient washing of the pyroantimoniate.

Antimony was weighed either as metal in powder or on platinum, as sulphide or as tetroxide, Sb_2O_4.

Arsenic was weighed either as mirror obtained by the Marsh test or as sulphide. Two mirrors of arsenic were estimated baroscopically.

Organ.	Weight in grams.	Antimony weighed as	grams.	Antimony calculated to grams.	Antimony calculated as tartar emetic.
Stomach and contents	130	Sb	0.0307	0.03070	0.08404
Intestines and contents	898	Sb	0.0042	0.00936	0.02562
	47	Sb_2S_3	0.0072		
Liver, spleen, and fluid from abdomen.	988	Sb_2O_4	0.1442	0.11423	0.31314
	?				
Heart	224	Sb_2O_4	0.0028	0.00221	0.00605
Kidneys	315	.....	.....	.....	.....
Brain	820	Sb_2O_4	0.0003	0.000237	0.00065
Muscle	227	Sb_2O_4	0.0004	0.000317	0.00086
				0.157054	0.43036

equivalent to 6.64 grains.

Organ.	Weight in grams.	Arsenic weighed as	grams.	Arsenic calculated to As.	Arsenic calculated to As_2O_3.
Stomach and contents	130	As_2S_3	0.0063	0.00384	0.00507
Intestines and contents	898	As_2S_3	0.1888	0.11512	0.15196
	47				
Liver, spleen, and fluid from abdomen	988	As_2S_3	0.1134	0.06914	0.09127
	?				
Heart	224	As	0.0003	0.00030	0.000396
Kidneys	315	As	0.0580	0.05800	0.07656
Brain	820	As	0.0002 estimated.	0.00020	0.000264
Muscle	227	As	0.0001 estimated.	0.00010	0.000132
				0.24670	0.325652

equivalent to 5.02 grains.

It was deemed important to produce evidence before the jury to confirm the statement that both antimony and arsenic existed in the viscera of the body exhumed. To this end the antimonial and arsenical compounds isolated from the several viscera were brought into weighable form. After weighing, these compounds were submitted to special tests, the results of which in many in-

stances were reserved as *corpora delicti*. These consisted in the case of

The Stomach of antimony as metal from the cyanide fusion; antimony on platinum and on tin; the oxide and the sulphide.

Bunsen tests, metal, sulphide, and reaction of oxide with silver nitrate and ammonia.

The arsenic was shown as a mirror obtained by Fresenius and von Babo's method. (No antimony could be detected in the fused mass of cyanide.) Arsenious sulphide and silver arsenate were also presented as exhibits.

The Intestine. Antimony was shown as metal on platinum and as sulphide; arsenic as Marsh test mirror and oxide; also the resulting mirror of a Marsh test using electyolysis; further, a Reinsch deposit on copper and a sublimate of arsenious oxide therefrom; silver arsenite, copper arsenite, arsenious sulphide, silver arsenate, magnesium ammonium arsenate and Bettendorff's test with stannous chloride.

The Liver, Spleen, and Fluid.—Antimony was shown by Marsh test, metal, silver antimonide and oxide; deposit from hydrogen antimonide on potassium hydroxide; antimonious sulphide, antimonic oxide, antimonious oxychloride, the metal on platinum and on tin; Bunsen's flame tests, metal and sulphide; Reinsch's test, metal and sublimate.

Arsenic, by Marsh test, elementary and oxide; deposit made from passing hydrogen arsenide over potassium hydroxide; silver and copper arsenates.

The Heart and Blood.—Antimony was shown as metal and sulphide; arsenic, as Marsh mirror.

The Brain.—Antimony was shown as sulphide; arsenic, as Marsh mirror.

The Muscle.—Antimony was shown as sulphide; arsenic, as Marsh mirror.

The Marsh test was conducted with the usual precautions and using zinc, slightly platinized, and sulphuric acids of varying strengths.

The apparatus was modeled after that proposed by Prof. R. Ogden Doremus, in 1859, and used in the trial of The People vs. James Stephens, since which date no other case of criminal poisoning by arsenic has been tried in New York City, until the

one now under consideration. At a subsequent date, 1878, the same observer, made another change during an investigation of a case where attempt to poison by antimony was charged, *viz.*, The People of the State of New Jersey vs. Rev. Geo. B. Vosburgh. Dragendorff's statement of the decomposability of hydrogen antimonide by stick potassium hydroxide was then verified, but his other statement that hydrogen arsenide does not undergo change was then disproved. This observation has been corroborated by Johnson and Chittenden[1] and in this case.

Dragendorff,[2] in his fourth edition which has just come to hand, modifies his statement concerning the decomposability of hydrogen arsenide by stick potassium hydroxide and refers to work done by Kühn and Säger in this connection. The quotation in the footnote shows that they were anticipated in this matter by R. Ogden Doremus.

Repeated experiments with various kinds of stick sodium and potassium hydroxides have been made since 1878, and though the darkening by arsenic is not as pronounced as with antimony, there is abundant evidence of it. The stains fade more readily. To avoid the loss of arsenic therefore, it has been customary with us to use fragments of pure caustic lime as a drying agent. These at least show no outward sign of a decomposition of either hydrogen antimonide or arsenide.

A small Erlenmeyer flask, well cooled and having granulated zinc within, had acid and when purged of air acid and suspected liquid fed into it from a stop-cock funnel. The escaping gas was dried by a layer of quick-lime between cotton plugs, and then conducted through several inches of hard glass tubing coiled in a spiral, surrounded by a hood and heated by a strong Bunsen flame. The escaping gas was conducted into a solution of silver nitrate.

A complete decomposition of the hydrogen arsenide occurs, no mirror appearing on a second coil, which may be added for precaution. Some of the Marsh tests were conducted with the view of weighing the mirrors, which was done except with the brain

[1] Dragendorff, *op. cit.*, 406; Otto, *op. cit.*, 198; Fresenius' System of Quantitative Chemical Analysis; Am. Ed. 1881, p. 782. "Otto and also Dragendorff recommend to pass the gas first over fragments of caustic potassa. We find, however, in accordance with Doremus, that arsenic is arrested by caustic alkali. S. W. J. and R. H. C."

[2] Dragendorff Ermittelung von Giften, vierte Auflage, 386 and 410.

and muscle, where they are so small as to render their retention as exhibits of greater importance than the ascertaining of their weight.

In other cases the Marsh test was used as a proof of the assertion that antimony and arsenic had been isolated. This last was particularly the case in the liver tissue, from which considerable quantities of each poison had been separated. A potassium hydroxide tube was therefore inserted instead of the quicklime, and well-defined black deposits obtained not only on the hydroxide but by the heated coil with antimony and arsenic, the antimonial deposit formed by the action of heat being on the side towards the generator, that of the arsenic beyond the heated spiral.

The arsenical deposit on the hydroxide is therefore of special interest.

Wormley[1] and others lay stress on the fact that the arsenical mirror forms beyond the heated portion of glass.

While conducting a Marsh test by the electrolytic evolution of hydrogen a gradual weakening of the current caused a gradually diminishing flow of gas.

A mirror of the character of those of arsenic formed on each side of the heated spiral. That these were both arsenical was proved by their being soluble in sodium hypochlorite solution, as well as from the extreme care taken to separate antimony from arsenic before employing the latter in the Marsh test.

Antimonious oxide occurs not only as valentinite but as prisms in exetele and as octahedra in senarmontite. The latter resembles ordinary arsenious oxide, a beautiful example of isodimorphism.

Just beyond the hotest part of a spiral employed in making a Marsh test for antimony we observed a crystalline deposit. The crystals were transparent octahedra, did not sublime when the tube was heated, and became red when acted on by hydrochloric acid and then ammonium sulphide. We have therefore apparently an instance of antimonious oxide depositing in the usual octahedral form of arsenious oxide.

Where admissable on account of quantity of arsenic or antimony at our disposal, the gases generated in the Marsh test were

[1] Micro-chemistry of poisons, 229, *1885*.

conducted through a silver nitrate solution before heating the spirals.

Though a darkening of the liquid was obtained in each instance, no arsenical reaction could be obtained from the liquid where the suspected antimonial solution was being added to the generator, nor antimony from the black deposit, where a supposably arsenical solution was under test. Antimony and arsenic revealed themselves however in the deposits in the former and in the liquid in the latter, a further evidence that a thorough separation of the two poisons had been effected in the analysis.

The statement is made that selenium hydride yields a black stain to glass at the heated portion, the stain remaining black as long as the glass is hot, but becoming invisible or white in character when the glass cools. We have verified this by experiments made with sulphuric acid containing selenium, a kind of acid not difficult to secure nowadays. Indeed, much sulphuric acid sold as chemically pure should be rejected for toxicological work solely on this ground. This dark stain on the glass is quite distinct from the one alluded to by Wormley[1] as due to arsenic in the glass or to the reddish-brown deposit given by selenium hydride when this gas is tested by the Marsh-Berzelius method. In connection with special tests, we desire to draw attention to the great delicacy of the flame tests when conducted by the methods suggested by Bunsen. We have had occasion to use them in a number of toxicological cases with marked success. In the Vosburgh case many of the exhibits shown were obtained with very small quantities of antimony by these means. Specimens of both antimonial and arsenical reactions were obtained in this investigation and formed part of the exhibit. As a rapid method of bedside testing, these reactions are most excellent. A small sliver of mica is a good substitute for asbestos fiber, and the suspected material can be readily introduced into a small reduction flame of either a Bunsen burner or alcohol lamp, while the oxide tests may be secured with the aid of a candle flame. A bit of china is a good substitute for a capsule, and may be used to catch the deposits by either crushing down the flame or holding it a little distance above it. The deposits may then be tested with suitable reagents.

[1] Wormley, *op. cit.*, 319 and 290.

As an adjunct to the Marsh test for arsenic, when a good-sized mirror had been obtained from a portion of the arsenic, extracted from the intestine, the hydrogen apparatus was removed and dry oxygen obtained by electrolysis was slowly passed in the reverse direction to the hydrogen current. The mirror was then gently heated at the side nearest the coil and the current of oxygen drifted the arsenious oxide formed through the first cold portion beyond where beautiful octahaedral crystals were formed.

Although the work thus outlined had been conducted with the assistance of Prof. John A. Mandel, who is jointly entitled to any credit belonging thereto, yet to anticipate certain legal quibbles, the District Attorney, Mr. De Lancey Nicoll deemed it expedient to submit a portion of the viscera for analysis to some one entirely unfamiliar with the history of the case. Prof. R. H. Chittenden was therefore requested to make an independent analysis of the kidneys, which resulted in his finding both antimony and arsenic. The former was in unweighable quantities. The arsenical mirrors obtained from the 315 grams of the kidneys weighed 0.0058 grams.[1] Prof. Chittenden then came to New York and together we analyzed the heart, finding antimony and arsenic as previously stated. The results of his analyses of the kidneys made a separate exhibit which he presented before the jury in his direct examination as a witness.

The defense did not dispute the finding of arsenic and antimony but attempted to show the impossibility of determining whether these poisons had not been introduced by some means after death. The medical history of the case, the condition of the body at the autopsy, the results of the pathological examination, and finally those of the chemical analysis were deemed sufficiently conclusive to the minds of the experts for the prosecution, to make special tests to elucidate this claim uncalled for. No testimony was produced by the defense to show that anyone had so introduced the poisons or had a motive to do so.

During the summing up by the defense, one of the jurors suddenly became insane. It was a recurrence of mental aberration

[1] The entire record of the case will be published under the direction of Assistant District Attorney John E. McIntyre.

which was totally unexpected. He had denied ever having had any mental disease when catechised previous to his acceptance as a juror. A second trial was therefore necessary. It resulted in a verdict of imprisonment for life.

The wife of the prisoner was held in custody for many months, but was finally released on her own recognizance. She had presented herself at the insurance offices dressed in appropriate mourning and claiming to be the widow of "Baum." Several of the companies made payments which she accepted.

It is a noteworthy circumstance that the history of antimonial poisoning is so frequently connected with the destruction of lives heavily insured. Taylor,[1] in a monograph, gives some remarkable cases. In some of these a second poison was administered. Though there have been cases where arsenic has been found along with antimony its presence has been due to the impure nature of the antimony. We have not been able to find the record of any case of chronic antimonial poisoning followed by the use of arsenic as a toxic agent.

BELLEVUE HOSPITAL MEDICAL COLLEGE,
May 10, 1895.

[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. NO. 4.]

ACTION OF HYDROCHLORIC ACID GAS UPON SALTS OF THE ELEMENTS OF GROUP V OF THE PERIODIC SYSTEM.

BY EDGAR F. SMITH AND JOS. G. HIBBS.

Received May 3, 1895.

IN a former number of this Journal (*Vol. XI, 578*) we took occasion to call attention to the rather interesting behavior of sodium vanadate, when gently heated in an atmosphere of hydrochloric acid gas. The results obtained by us proved that vanadic acid is entirely expelled from its salt by this means. This behavior naturally suggested a line of investigation, which we hoped to begin at once, but it was not until very recently that we were able to resume the study. The idea as to whether the salts of the acids of other elements of Group V of the Periodic System were similarly transposed by hydrochloric acid gas, or by the gaseous haloid acids in general, constantly obtruded itself.

[1] On Poisoning by Tartarized Antimony. A. S. Taylor, M.D., F.R.S., Guy's Hospital Reports, Third Series, **3**, 369, *1857*.

We accordingly turned to sodium nitrate and submitted it to the action of hydrochloric acid gas, aiding the reaction by a gentle heat. The gas was evolved by dropping concentrated sulphuric acid from a funnel tube into commercial hydrochloric acid. From the evolution flask it passed through an empty bottle and then through sulphuric acid, from which it entered a combustion tube carrying a boat containing the salt to be acted upon. The products of the reaction were conducted into water, contained in a bulb-receiver, to which was attached a small Erlenmeyer flask containing water.

When the gas came in contact with pure sodium nitrate, action set in even in the cold. The salt assumed a brown-yellow color and a yellow liquid condensed in the cooler portion of the combustion tube. On the application of heat this was driven into the receiver. The action was continued for fifteen minutes, after which the boat was allowed to cool in the gas and then transferred to a vacuum desiccator, where it remained for an hour before it was weighed. An examination of its contents revealed the presence of nothing but sodium chloride. That the conversion was quantitative is evident from the following data:

Experiment 1.—0.1878 gram of carefully dried nitrate gave 0.1289 gram of sodium chloride, while the calculated quantity of the latter is 0.1290 gram.

Experiment 2.—0.3536 gram of nitrate gave 0.2429 gram of chloride, instead of the theoretical 0.2428 gram.

Experiment 3.—0.2971 gram of nitrate gave 0.2040 gram of chloride, while the required quantity is 0.2041 gram.

Experiment 4.—0.6462 gram of nitrate gave 0.4440 gram of chloride, instead of 0.4439 gram, as required by theory.

In experimenting with phosphates we used pure sodium pyrophosphate. We found that this salt was not affected when subjected to the action just described. Nothing was expelled from it. When sodium pyroarsenate was substituted for the phosphate action did occur; the arsenic was completely volatilized and collected in the water contained in the bulb-receiver. The contents of the latter were carefully poured into a beaker glass and oxidized with a few drops of nitric acid. Later a "magnesia mixture" was added to the neutralized solution, which was permit-

ted to stand fifteen hours before the magnesium ammonium arsenate was filtered. It was finally weighed as magnesium pyroarsenate. The contents of the boat were also dissolved and tested for arsenic, but none was found.

Experiment 1.—0.3844 gram of sodium pyroarsenate gave 0.3355 gram of magnesium pyroarsenate, instead of 0.3361 gram, the quantity required by theory.

Experiment 2.—0.1093 gram of sodium pyroarsenate gave 0.0959 gram of the magnesium salt, instead of 0.0956 gram, the calculated quantity.

In these experiments a colorless liquid collected in the cooler portions of the tube beyond the boat, but this disappeared upon the application of a gentle heat.

In a third trial the aqueous arsenic solution was not oxidized, consequently the arsenic obtained by precipitation with the "magnesia mixture" was far from the required quantity. From this we infer that the arsenic is not volatilized wholly as a derivative of its higher oxide. The latter doubtless suffers partial reduction. We are striving at present to ascertain in what form it is removed. When it is considered that vanadic acid is expelled as an oxychloride, analogy would suggest some similar form for the arsenic. Of this, however, we expect to speak more definitely in the future.

Care should be exercised in heating the sodium pyroarsenate in the hydrochloric acid gas, as the salt when heated in it fuses very readily, and after fusion sets in the acid acts rather slowly. Magnesium pyroarsenate and lead arsenate were found to be converted quite as readily, by the gas, into their chlorides and the arsenic as completely eliminated as in the case of the sodium salt. The corresponding phosphates remained unchanged.

The separation of the two acids, when associated as sodium salts, as magnesium salts, and lead salts, was tried.

Experiment 1.—A mixture, consisting of one-tenth gram of sodium pyroarsenate and an equal amount of sodium pyrophosphate, was treated as just described. The arsenic found in the bulb-receiver and weighed as magnesium pyroarsenate, was 0.0869 gram. Theory required 0.0874 gram. The phosphate remaining in the boat was dissolved in water and the acid finally

weighed as magnesium pyrophosphate. It equaled 0.0830 gram instead of 0.0834 gram, the theoretical quantity.

Experiment 2.—In this trial 0.1100 gram of each salt was used. The volatilized arsenic, weighed as pyro-salt, equaled 0.0957 gram, instead of 0.0961 gram. The non-volatilized phosphorus, weighed in the same form, equaled 0.0909 gram, instead of the theoretical 0.0918 gram.

We next prepared magnesium pyroarsenate and magnesium pyrophosphate. Mixtures of these salts were then acted upon by the acid gas. Two separations were made with the following results:

Experiment 1.—0.1100 gram of each salt brought into a boat was acted upon by the acid. No difference from the behavior of the sodium salts was observed, excepting that the tendency to fusion was not so marked in this case as with the sodium salts. The volatilized arsenic acid gave 0.1094 gram of magnesium pyro-salt, thus falling short of the theoretical amount by 0.0006 gram. The residual magnesium pyrophosphate weighed 0.1105 gram. This approaches the theoretical (0.1100 gram) so closely that the separation must be viewed as complete.

Experiment 2.—The same quantities of the two salts were taken in this trial. Instead of 0.1100 gram of pyrophosphate actually taken the found salt equaled 0.1108 gram. The difference between the arsenic salt used and the quantity of it, which was carried out of the mixture by the gas, equaled 0.0009 gram. An examination of the non-volatilized phosphate showed it to be free from arsenic. Lead arsenate was very readily transposed by the acid into lead chloride, and the volatile arsenic derivative.

	Lead arsenate.	Lead chloride. Obtained.	Required.
Experiment 1.—	0.2965 gram gave	0.2746 gram	0.2747 gram.
" 2.—	0.3608 " "	0.3347 "	0.3343 "

The residual lead chloride was dissolved in water, and the aqueous solution introduced into a Marsh apparatus. Not a trace of arsenic was found in this way. Upon adding a very slight amount of lead arsenate to the solution the mirror and spots of arsenic were almost immediately observed. The complete transposition of this salt induced us to execute a third trial in which we not only weighed the residual lead chloride and

found it satisfactory, but also determined the arsenic which had been volatilized.

Lead arsenate.	Magnesium pyroarsenate. Found.	Calculated.
0.2965 gram gave.....	0.1022 gram.	0.1028 gram.

Two portions of a mineral containing lead, arsenic acid, and phosphoric acid, were exposed to the action of the acid gas. The volatilized arsenic equaled in (a) 10.42 per cent, and in (b) 10.39 per cent. None remained in the residue contained in the boat.

Experiments have not yet been made with antimonates.

Separations of vanadic and arsenic acids from tungstic and chromic acids are now being carried out, and with encouraging results. The action of hydrobromic, hydriodic and hydrofluoric acid in gas form upon vanadates, nitrates, arsenates and phosphates, has received attention with results which will appear later.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. NO. 5.]

URANIUM OXYNITRIDE AND URANIUM DIOXIDE.

BY EDGAR F. SMITH AND J. MERRITT MATTHEWS.

Received May 31, 1895.

THE action of ammonia upon molybdenyl (MoO_2Cl_2) and tungstyl (WO_2Cl_2) chlorides has received attention in this laboratory. To complete the study of Group VI in this direction, uranyl chloride (UO_2Cl_2) was prepared, placed in a porcelain boat and heated in a glass tube in a current of dry ammonia. At a comparatively moderate temperature the material began to take on a dark color, and copious fumes of ammonium chloride were evolved. The heat was raised and continued until the ammoniacal salt was no longer produced. The residue was dull black in color. When fused in a nickel crucible with caustic potash, ammonia was slowly evolved. A portion of the substance introduced into aqueous silver nitrate caused the separation of a beautiful deposit of brilliant crystals of metallic silver. Chlorine was not found in the compound. When it was heated with sulphuric acid (1 : 2) in a sealed tube, complete solution ensued. Upon titration with standardized potassium permanganate, the presence of 6.83 per cent. of dioxide was disclosed. No hydro-

gen was discovered in the material examined for it. Four analyses were made and resulted as follows:

0.2311	gram	of	material	gave	84.81	per cent.	uranium.
0.3139	"	"	"	"	2.19	" "	nitrogen.
0.2412	"	"	"	"	84.87	" "	uranium.
0.1868	"	"	"	"	2.24	" "	nitrogen.

The mean of the uranium and nitrogen determinations was 84.84 per cent. uranium and 2.21 per cent. nitrogen, leaving a difference of 12.95 per cent. for oxygen. The formula we have deduced from these figures is $U_{11}N_5O_{25}$, which requires 84.88 per cent. uranium, 2.25 per cent. nitrogen, and 12.87 per cent. oxygen.

Uhrlaub[1] mentions an oxynitride of uranium which from its analysis approximates the formula $U_9N_4O_{18}$.

From further experiments made by us it is evident that these oxynitrides are bodies of extremely variable constitution, dependent upon the temperature and length of time to which the uranium body is exposed to the action of the ammonia. This conduct was also observed to prevail with the corresponding derivatives of both molybdenum and tungsten.

Preparation of Uranium Dioxide.—The preparation of this compound has been the subject of much discussion. It will be remembered that this is the oxide long looked upon as metallic uranium. Zimmermann[2] found that it resulted upon merely heating the oxide U_3O_8 in indifferent gases, such as carbon dioxide. Others have recommended the ignition of urano-uranic oxide in hydrogen, or together with sulphur, or with sulphur and ammonium chloride. We submit the course by which we obtained it. The oxide U_3O_8 was intimately mixed with a large excess of dry ammonium chloride in a porcelain crucible, and this then placed in a larger Hessian crucible and surrounded with closely packed charcoal. The crucibles were heated in a wind furnace at almost a white heat for about six hours. A reddish brown substance remained. It contained no nitrogen or chlorine. Two portions of it were dissolved in nitric acid and the uranium determined with these results: 88.23 per cent. and

[1] Verbindungen einiger Metalle mit Stickstoff, Göttingen, 1859.
[2] Annalen, **232**, 283.

88.00 per cent., giving as a mean 88.12 per cent. A third portion, weighing 0.3363 gram, was heated for fifteen minutes over a Bunsen flame; the increase in weight was 0.0119 gram, and heating again for forty-five minutes there resulted an alteration of only 0.0011 gram, after which the weight continued constant. The total increase of the material taken by its conversion into urano-uranic oxide, was therefore 0.0130 gram, while the calculated increase should be 0.0132 gram.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. NO. 6.]

THE SEPARATION OF IRON FROM BERYLLIUM.

BY ELIZABETH A. ATKINSON AND EDGAR F. SMITH.

Received May 31, 1895.

THIS separation is generally effected through the solubility of beryllium hydroxide in ammonium carbonate. It is, however, not always satisfactory, and any method affording better results will be of interest to the analyst.

Ilinski and v. Knorre[1] called attention to the use of nitroso-β-naphthol in analytical work. For example, they separated cobalt from nickel and iron from aluminum by means of this reagent. Inasmuch as their study has not been continued, it seemed to us of interest to ascertain whether or not the same reagent could be used for the separation indicated at the head of this communication. We used the following solutions: (1) a fifty per cent. acetic acid solution of the nitroso-β-naphthol, (2) a ferric solution of which ten cubic centimeters contained 0.1278 gram of ferric oxide, and finally a beryllium chloride solution of which ten cubic centimeters contained 0.1248 gram.

The first step taken was to learn how completely the iron was precipitated by the proposed reagent. To this end ten cubic centimeters of the ferric solution ($=0.1278$ gram Fe_2O_3) were diluted with two hundred cubic centimeters of distilled water, and one hundred and twenty-five cubic centimeters of the nitroso-β-naphthol added to the cold liquid, which was then allowed to stand for a period of twenty-four hours. The iron precipitate was then filtered out, washed at first with fifty per cent. acetic acid, and subsequently with water, until a few drops of the washings left no residue upon evaporation and ignition upon a strip

[1] *Ber. d. chem. Ges.*, **18**, 699, 2728.

of platinum. After the iron nitroso-β-naphthol had dried it was mixed with an equal amount of pure oxalic acid, and the filter folded up over the mixture, which was then carefully heated in a weighed porcelain crucible. The heat at first was moderate, but gradually increased until all the carbon had been burned off. These are practically the precautions which were recommended by Ilinski and v. Knorre, so that our experience corroborates that given by these chemists.

The results obtained by us are:

1. 0.1277 gram of ferric oxide.
2. 0.1283 " " " "
3. 0.1277 " " " "

The theoretical ferric oxide equaled 0.1278 grams.

Upon treating ten cc. of the beryllium solution just as described under the iron, no evidence of precipitation was observed even after the expiration of forty-eight hours.

The real object of our study was the separation of the iron from the beryllium. In following out this idea we proceeded in the following manner: Ten cc. of the ferric salt (=0.1278 gram of ferric oxide) and an equal volume of the beryllium solution, equal to 0.1248 gram beryllium oxide, were diluted to two hundred cc. with distilled water. The nitroso-β-naphthol solution was added to this cold mixture. After standing twelve hours the ferric compound was filtered out and disposed of as above described. The ferric oxide found was:

1. 0.1277 gram,
2. 0.1275 "
3. 0.1277 "

instead of the theoretical 0.1278 gram.

Efforts made to precipitate uranium salts with this reagent resulted negatively. The substitution of an alcoholic for an acetic acid solution of the reagent made no difference.

We also found that nitroso-β-napthol does not precipitate solutions of cerous salts, of lanthanum ammonium nitrate, of praseodymium nitrate, of neodymium nitrate, of terbium, of erbium, or of sodium molybdate or tungstate. Zirconium chloride gave an orange-colored precipitate, and ceric ammonium nitrate a bright scarlet, flocculent precipitate, which was, however, far from being complete.

UNIVERSITY OF PENNSYLVANIA.

ON THE VAPOR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.

By C. E. Linebarger.

[*Continued from page 652*]

Table VII.

Vapor-Tensions of Mixtures of Toluene and Chloroform at 34.8°.

Vapor-Tension of Toluene at 34.8° is 46.8 mm. of Mercury.

Vapor-Tension of Chloroform at 34.8° is 289.2 mm. of Mercury.

Molecules $CHCl_3$ in 100 molecules of liquid mixture.	Molecules $CHCl_3$ in 100 molecules of gaseous mixture.	Grams $CHCl_3$ in vapor.	Grams C_7H_8 in vapor.	Tension of $CHCl_3$ in mm.	Tension of C_7H_8 in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
28.74	65.29	0.4856	0.1994	64.7	34.4	1040	747	24
60.43	89.20	1.3578	0.1270	160.9	19.5	1031	754	23

Table VIII.

Vapor-Tensions of Mixtures of Benzene and Carbon Tetrachloride at 34.8°.

Vapor-Tension of Benzene at 34.8° is 145.4 mm. of Mercury.

Vapor-Tension of Carbon Tetrachloride at 34.8° is 169.4 mm. of Mercury.

Molecules CCl_4 in 100 molecules of liquid mixtnre.	Molecules CCl_4 in 100 molecules of gaseous mixture.	Grams CCl_4 in vapor.	Grams C_6H_6 in vapor.	Tension of CCl_4 in mm	Tension of C_6H_6 in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
7.21	9.66	0.1741	0.8260	14.5	135.4	1205	762	18
18.68	20.54	0.3931	0.7561	32.5	125.5	1205	758	20
28.00	35.71	0.6267	0.5730	60.0	105.0	1016	756	12
50.19	55.03	1.1231	0.4666	91.3	75.6	1201	762	19
63.88	65.27	1.2699	0.3431	103.1	54.5	1219	760	27
77.89	83.01	1.5321	0.1669	117.6	31.8	1034	754	26

Table IX.

Vapor-Tensions of Mixtures of Toluene and Carbon Tetrachloride at 34.8°.

Vapor-Tension of Toluene at 34.8° is 46.8 mm. of Mercury.

Vapor-Tension of Carbon Tetrachloride at 34.8° is 169.4 mm. of Mercury.

Molecules CCl_4 in 100 molecules of liquid mixture.	Molecules CCl_4 in 100 molecules of gaseous mixture.	Grams CCl_4 in vapor.	Grams C_7H_8 in vapor.	Tension of CCl_4 in mm.	Tension of C_7H_8 in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
30.69	58.19	0.4754	1.2046	51.5	37.0	1016	756	12
53.85	67.86	0.9305	0.1260	78.3	22.3	1022	758	17
60.00	83.67	0.9624	0.1126	99.1	19.4	1020	759	14
91.87	97.22	1.6063	0.0281	155.1	4.5	1017	756	13

TABLE X.

Vapor-Tensions of Mixtures of Nitrobenzene and Carbon Tetrachloride at 34.8°.

Vapor-Tension of Nitrobenzene at 34.8° is 1.16 mm. of Mercury.

Vapor-Tension of Carbon Tetrachloride at 34.8° is 169.4 mm. of Mercury.

Molecules CCl_4 in 100 molecules of liquid mixture.	Molecules CCl_4 in 100 molecules of gaseous mixture.	Grams CCl_4 in vapor.	Grams $C_6H_5NO_2$ in vapor.	Tension of CCl_4 in mm.	Tension of $C_6H_5NO_2$ in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
5.37	93.51	0.3095	0.0175	18.9	1.3	1973	760	20
50.73	94.47	1.1111	0.0489	113.9	6.2	1020	756	12
73.54	96.09	1.4420	0.0471	141.5	5.6	1022	753	18
95.21	98.61	1.7798	0.0190	167.6	2.3	1022	753	18

10. INFLUENCE OF TEMPERATURE ON THE VAPOR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.

It is a well-known fact that the higher the temperature the greater the vapor-tension; this is true of mixtures of liquids as well as of the liquids themselves. It may be, now, that the vapor-tensions of mixtures of volatile liquids exhibit a deportment varying with the temperature; but if it can be shown that change of temperature is without influence upon the nature of the phenomenon presented by the vapor-tensions of such mixtures, the experimental investigation of the subject is much simplified, for theoretic conclusions based on data found at a certain temperature can be at once applied to other temperatures, so that the investigation of the vapor-tensions of mixtures of various concentrations at one temperature suffices for the discussion and elucidation of the entire problem. Material which furnishes an answer to the question as to whether temperature has an influence upon the vapor-tensions of mix-

tures of volatile liquids can be found in the papers of Regnault (*loc. cit.*), Raoult (*loc. cit.*), and Brown (*loc. cit.*).

Regnault's determinations were made through a considerable range of temperature, and, although, at most only three different concentrations were examined, it is possible by rearranging them to get an answer to our query. The mixtures which can be utilized are five in number,—two mixtures of carbon bisulphide and ethyl oxide, whose vapor-tensions were determined by the static method, and one mixture of the same liquids, the vapor-tension of which was determined by the dynamical method; and two mixtures of carbon bisulphide and carbon tetrachloride of which the vapor-tensions were investigated by the static method.

The first mixture of carbon bisulphide and ether was made up of sixty-two volumes of the first liquid and thirty-eight volumes of the second, ("Mélange de 62 sulphure de carbone et 38 d'éther, en volumes"), and eleven determinations of its vapor-tension were made in the temperature interval 4.72° to 39.44°. If we put the specific gravity of Regnault's carbon bisulphide at 1.27, and that of his ether at 0.78, the mixture contained by weight 27.35 per cent. of ether, and 72.65 per cent. of carbon bisulphide; or a hundred molecules of the mixture contained 27.20 molecules of ether and 72.80 molecules of carbon bisulphide. The second mixture was prepared by mixing fifty-six volumes of ether and forty-one volumes of carbon bisulphide ("Mélanges de 56 éther et de 41 sulphure de carbone en volumes"). Thirteen determinations were made of the vapor-tensions of this mixture at temperatures varying from 8.01° to 38.18°. One hundred parts by weight contained then 45.61 parts of ether and 54.39 parts of carbon bisulphide; and one hundred molecules of the mixture contains 46.29 molecules of ether and 53.71 molecules of carbon bisulphide.

The third mixture of carbon bisulphide and ether was made up of equal volumes of each; ("Mélange, a volume éguax, de sulphure de carbon et d'éther") about twenty-five measurements were made in the temperature interval from 20.81° to 121.48°. The percentage composition of the mixture is 61.95 per cent. of carbon bisulphide and 38.05 per cent. of ether, and the molecu-

lar percentage composition is 61.32 molecules of carbon bisulphide and 38.68 molecules of ether.

The first mixture of carbon tetrachloride and carbon bisulphide contained equal volumes of the two liquids; ("Mélange de volumes égaux de chlorure de carbone et de sulphure de carbone") ten determinations of its vapor-tension were made at temperatures varying from 8.75° to 48.43°. If we put the specific gravity of Regnault's carbon tetrachloride as equal to 1.62, and that of his carbon bisulphide as equal to 1.27, the percentage composition by weight of the mixture is 56.06 per cent. of carbon tetrachloride and 43.94 per cent. of carbon bisulphide; and one hundred molecules of the mixture contain 61.2 molecules of the first-named liquid and 38.8 molecules of the last-named.

In indicating the composition of the second mixtures Regnault uses the following words: "Mélange de 60 parties sulphure de carbone et de 145 chlorure de carbone." There is doubt here as to whether Regnault means by "parties," parts by weight or by volume. This is the only place where this form of expression is used, and in the other cases, it is expressly stated that the units of measure are volumes. I take it, then, that in this case parts by weight are to be understood, and in the sequel it will be seen that the regularity of the data as represented graphically renders this understanding of the matter warranted. At any rate, the difference between the results of calculations with volumes or weights as bases is not very great, so that there is not much danger of committing any very gross error. By weight the percentage composition of this mixture is 70.73 per cent. of carbon tetrachloride and 29.27 per cent. of carbon bisulphide, while one hundred molecules of it contain 65.47 molecules of carbon tetrachloride and 34.53 molecules of carbon bisulphide. I give also the percentage molecular composition on the assumption that Regnault's "parties" means parts by volume; one hundred molecules of the mixture contain 54.47 molecules of carbon tetrachloride and 45.53 molecules of carbon bisulphide.

In order to transform Regnault's data, the following procedure was gone through with: In a system of coordinates with temperatures as abscissas and vapor-tensions as ordinates, his measurements were plotted on a large scale; as might be expected

of any of Regnault's experimental work, the points fell very close to a regular curve. At points at this curve corresponding to 0°, 10°, 20°, 30°, etc., the value of the ordinates was carefully taken, that is, the vapor-tensions for each of the above temperatures. In this way data were obtained by means of which isothermal curves were drawn in a system of coordinates with concentrations as abcissas and vapor-tensions as ordinates.

An inspection of the isothermal curves shows that no appreciable influence of temperature manifests itself; the vapor-tension of the more volatile component of the mixture increases, indeed, more rapidly than that of the less volatile, but this does not affect the contour of the curve, its inclination alone being somewhat altered.

Raoult[1] made a special study of the possible influence of temperature upon the vapor-tensions of mixtures of ether with each of the following liquids almost nonvolatile at low temperatures: turpentine, aniline, perchlorethane, and benzoic acid, the temperature interval being from 0° to 22°. The results of his experiments permitted him to draw the definite conclusion that in the above temperature interval the vapor-tension is quite independent of the temperature.

The experiments of Brown[2] on the boiling-points of carbon bisulphide and carbon tetrachloride may be brought forward as evidence that the influence of the temperature on the vapor-tensions of mixtures of normal liquids is very slight; he found the curves, sketched with percentage composition on the axis of abscissas, and boiling-points on the axis of ordinates, for the pressures 747 to 760, and 430 to 432 mm. to be practically parallel.

From the above considerations, we may conclude that temperature has but a vanishing influence upon the vapor-tensions of mixtures of normal liquids; that is to say, although the higher the temperature, the greater the vapor-tension, the regularities found and the laws deduced from observations made at any one temperature are, without question, applicable to any other temperature, which, however, be it remarked as a caution, should probably not be too different from that of the observations.

[1] *Loc. cit.*
[2] *Loc. cit.*

XI. RELATIONS BETWEEN THE VAPOR-TENSIONS, PARTIAL AND TOTAL, AND THE CONCENTRATION OF THE LIQUID PHASES.

We remark first, that the tension of the mixed vapor emitted by any of the mixtures of volatile liquids examined is always greater than the tension of the less volatile liquid and always less than that of the more volatile liquid; also, that the partial tension or pressure of either component, of any mixture, is always less than the vapor-tension of the component in a state of purity;[1] these two properties belong to all the mixtures investigated. In the discussion of the other properties, we shall find it convenient to divide the mixtures into classes. In the first class we put the mixtures of benzene and toluene with monochlor- and monobrombenzene; in the second, the mixtures of chloroform with benzene, and with toluene; in the third, the mixtures of carbon tetrachloride with toluene, and with benzene; and in the fourth and last, the mixture of nitrobenzene and carbon tetrachloride.

Now the mixtures of the first class are made up of liquids which are very similar in their chemical constitution, and it is natural to expect that they will exhibit the very simplest phenomena when mixed with one another. And, indeed, this expectation is realized, for the vapor-tensions of their mixtures are seen to be linear functions of the concentration: in the graphic representations (abscissas = molecular percentages; ordinates = vapor-tensions) of the determinations, these fall upon or very close to the straight lines connecting the points on the axes of ordinates corresponding to the vapor-tensions of each of the pure liquids. In order to find the vapor-tension of any mixture of these liquids, all that is necessary to do is to connect on the axis of ordinates, the points representing the vapor-tensions of the two liquids in a state of purity, by a straight line, and where the perpendicular to the axis of abscissas cuts this line, the value of the ordinate corresponding to the point of intersection gives

[1] This observation does not seem to be confirmed in the case of the partial pressure of nitrobenzene in its mixture with carbon tetrachloride. This exception, however, I am inclined to attribute to experimental errors, which made themselves particularly felt in the investigation of mixtures of these two liquids. Indeed, if the allowance be made for the degree of accuracy which we have decided the method capable of yielding, it will be seen that the discrepancy can be made to disappear almost entirely.

the vapor-tension of the chosen concentration; of course, partial tensions can be found in a similar way. Also, by the application of the "rule of mixtures," it is easy to calculate the total or partial tensions. It may be worth while to remark, in passing, that these four liquids, which we have put in a class by themselves, are just those which verify by far the best the generalizations of van der Waals; undoubtedly, these liquids are to be reckoned as in the highest degree "normal," as their behavior approaches most nearly that theoretically predicted.

In the second of our classes we find a different behavior. When chloroform is added to benzene or to toluene, the total vapor tension is less than that resulting from the calculation by the rule of mixtures; the variation reaches a maximum when 100 molecules of the mixture contain from fifty to sixty molecules of chloroform; the curve then tends to approach the straight line connecting the points on the axis of ordinates representing the vapor-tensions of the pure liquids, practically coinciding with it when the number of chloroform molecules has passed eighty. The depression of the vapor-tension of chloroform, caused by the addition of either benzene or toluene, is linearly proportional to the concentration only in solutions containing less than twenty molecules of either hydrocarbon to 100 molecules of the mixture.

When we consider the partial tensions of these mixtures, we see that the same regularity as was observed in the first class of liquids is found here, but only for toluene and benzene; the partial tension curve for chloroform resembles closely in its contour that for the total tension of the mixture. The departure of chloroform from the straight line is not, however, very marked.

In the third class of mixtures, we meet with a different behavior. When benzene or toluene is added to carbon tetrachloride, we observe that the curve of total tension follows closely the line connecting the points corresponding to the vapor-tensions of the mixed liquids until towards the abscissas value of eighty; the curve then commences to fall, only to rise again, and pass above the straight line, when, finally, it changes its direction to fall upon the axis of ordinates at the point standing for the vapor-tension of the pure hydrocarbon, benzene, or

toluene, as the case may be. As is seen, the curve has three turning points. The curve of the partial tension of the carbon tetrachloride resembles in every detail, in each mixture, that of the total tension; but once more it is observed that the partial pressure curve for the hydrocarbons is, so to say, a straight line. It is truly a remarkable result that in the mixtures which have such different total tension curves, the curve for these two liquids should turn out so simple. There is but little doubt that the above instances are sufficient to render very probable the assumption that this behavior is general, and that in all binary mixtures made up of benzene or toluene, with any other volatile liquid whatsoever, the same normality in the behavior as regards partial vapor-tension of these two hydrocarbons will be found. It is even possible to go a step farther, and claim that, inasmuch as in the mixtures of the first class, normality of the partial pressure was found in the case of each component of the mixture, this normality will persist in mixtures of the halogen compounds of benzene with any other liquids.

The fact that benzene and toluene possess "straight line" partial pressure curves will enable us to get reliable and important information as to the partial pressures of other liquids mixed with either of the hydrocarbons, from a knowledge of the total pressure of the mixtures; for all that is necessary to do is to draw, in the coordinate system adopted in this paper, the total pressure curve and a straight line from the point, representing, on the axis of ordinates, the vapor-tension of benzene at the temperature at which the determination has been made, to the foot of the opposite ordinate; the value of any ordinate comprised between these two curves gives, then, the partial pressure, to a very close approximation, of the other component of the mixture.

Furthermore, it is apparent that the partial tensions of either chloroform or carbon tetrachloride is the same when mixed in the same proportions with either benzene or toluene; the simplicity of the behavior of the latter liquids permits of the free exhibition of the peculiarities in that of the former.

The fourth class of mixtures, of which the only representative here is the mixture of nitrobenzene and carbon tetrachloride,

does not, in reality, belong to our subject of investigation, which is to study mixtures of volatile liquids only, and not those of a volatile with an almost involatile one. Still it was thought advisable to find out what the partial tensions of mixtures of such liquids would be, inasmuch as Raoult[1] has made an elaborate study of the total vapor-tension of mixtures of ether and several almost non-volatile liquids. As is seen in the curve, the partial pressure of the carbon tetrachloride and the total pressure of the mixture are almost identical, just as would naturally be expected. The curves are, if we regard the right-hand ordinate first, at the beginning parallel with the straight line connecting the points representing the vapor-tensions of the pure liquids; they then turn upwards, reach a maximum distance from the straight line at about the abscissas value of fifty, and then gradually turn downwards towards the origin. I was curious to see if this behavior was characteristic of the mixtures of liquids investigated by Raoult.

Accordingly, I have recalculated his data so as to get them into a form comparable with mine. These recalculated data are given in the following small tables:

TABLE A.

Vapor-Tensions of Solutions of Turpentine in Ether at 16.2°.
Vapor-Tension of Turpentine at 16.2° is four mm. of Mercury.
Vapor-Tension of Ether at 16.2° is 377 mm. of Mercury.

Molecules of turpentine in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of turpentine in 100 molecules of solutions.	Vapor-tension in mm. of mercury.
5.9	354	35.5	255
12.1	332	47.9	212
23.4	294	64.5	159

TABLE B.

Vapor-Tension of Solutions of Nitrobenzene in Ether at 16.0°.
Vapor-Tension of Nitrobenzene at 16.0° is four mm. of Mercury.
Vapor-Tension of Ether at 16.0° is 374 mm. of Mercury.

Molecules of nitrobenzene in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of nitrobenzene in 100 molecules in solution.	Vapor-tension in mm. of mercury.
6.0	353	56.2	232
17.9	321	75.9	166
35.5	278	84.0	132

[1] *Loc. cit.*

TABLE C.

Vapor-Tensions of Solutions of Aniline in Ether at 15.3°.
Vapor-Tension of Aniline at 15.3° is four mm. of Mercury.
Vapor-Tension of Ether at 15.3° is 364 mm. of Mercury.

Molecules of Aniline in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of Aniline in 100 molecules of solution.	Vapor-tension in mm. of mercury.
3.8	349	20.5	292
7.7	335	49.6	210
14.8	308	68.7	147

TABLE D.

Vapor-Tension of Solutions of Methyl Salicylate in Ether at 14.2°.
Vapor-Tension of Methyl Salicylate at 14.2° is four mm. of Mercury.
Vapor-Tension of Ether at 14.2° is 306 mm. of Mercury.

Molecules of methyl salicylate in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of methyl salicylate in 100 molecules of solution.	Vapor-tension in mm. of mercury.
1.1	344.6	23.2	281
2.1	343.6	49.0	208
4.8	332.0	77.0	125
9.2	316.0	85.0	101
15.1	301.0	....	....

TABLE E.

Vapor-Tensions of Solutions of Ethyl Benzoate in Ether at 11.7°.
Vapor-Tension of Ethyl Benzoate at 11.7° is three mm. of Mercury.
Vapor-Tension of Ether at 11.7° is 313 mm. of Mercury.

Molecules of ethyl benzoate in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of ethyl benzoate in 100 molecules of solution.	Vapor-tension in mm. of mercury.
4.9	296	53.0	167
9.6	286	75.5	94
27.1	235	94.4	39

If these results be plotted in a system of coordinates, the curves will be found to have a close resemblance to the one which I have found for the mixture of nitrobenzene and carbon tetrachloride. It seems likely that this form of curve is the general one for the total tension of mixtures of a volatile with an almost fixed liquid.

XII. RELATIONS BETWEEN THE CONCENTRATIONS IN THE GASEOUS AND LIQUID PHASES.

The relations between the concentration in the gaseous and liquid phases is clearly shown by curves drawn in a system of coordinates, of which the axis of abscissas is taken for the rep-

resentation of the molecular percentage composition of the liquid phase, and the axis of ordinates for that of the gaseous phase. In Fig. V are drawn these curves, the data being taken from the first two columes of tables.

As is seen, the curves prove to be very regular, and group themselves on either side of the diagonal of the square, according as the component chosen to increase from left to right in the diagram is more or less volatile than the other; as this was taken to be the component containing a halogen, the curve is below the straight line when the halogen-containing liquid is less volatile than the other, and above, when it is more volatile.

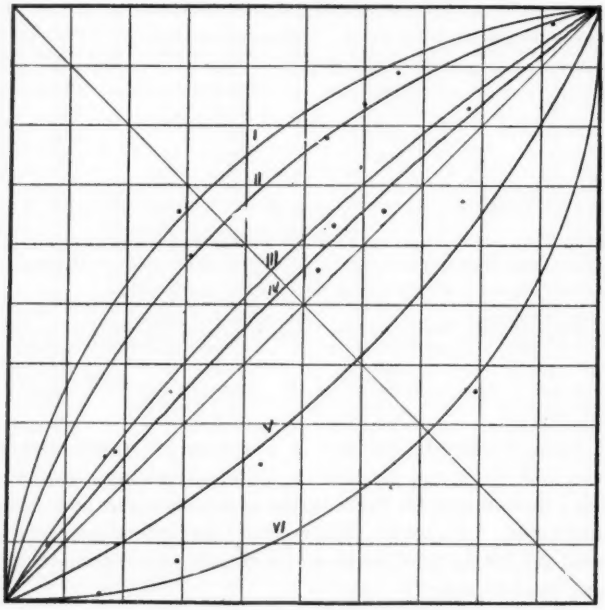

FIG. 5.—RELATIONS BETWEEN THE CONCENTRATIONS IN LIQUID AND GASEOUS PHASES.

Abscissas = molecules of one liquid in 100 molecules of mixture of liquids.
Ordinates = molecules of one vapor in 100 molecules of mixture of vapors.

Curve I.....Toluene-chloroform.
" II.....Toluene-carbon tetrachloride.
" III.....Benzene-chloroform.
" IV.....Benzene-carbon tetrachloride.
" V.....Toluene-monochlorbenzene.
" VI.....Benzene-monochlorbenzene.

Furthermore, the greater the difference in the volatility of the two liquids in the mixture the greater the curvature. It is very probable that mixtures of two normal liquids with the same vapor tension would give off vapors with identical composition in both liquid and gaseous state.

XIV. HEAT OF DILUTION AND SOLUTION. IDEAL CONCENTRATED SOLUTIONS.

Kirchoff[1] developed by thermodynamic considerations an equation showing a relation betweenthe heat of dilution of a solution and its vapor-tension. If we designate by dQ the heat brought into play when the small quantity dm of water is added to the solution, and if p' represent the vapor-tension of the solution and p that of the pure solvent, while T is the temperature and R the gas constant measured in units of heat, he found that

$$\text{(A)} \qquad \frac{dQ}{dm} = RT^2 \frac{k \log \frac{p'}{p}}{dT}$$

This equation was more particularly developed for the case of solutions of fixed substances, and has in fact been compared with the experiments done on the vapor-tensions and heat of dilution of sulphuric acid dissolved in water. Recently, however, three quite similar formulas have been obtained which apply directly to the heat given out or taken in when two liquids are mixed, and the corresponding changes of the elastic forces of the vapors. LeChatelier[2] developed for the case of a mixture of two liquids the formula

$$\text{(B)} \qquad n \frac{dp}{p} + n' \frac{dp'}{p'} - 500 \frac{n L_1 + n' L_2 + \lambda}{T^2} dT = 0$$

wherein p and p' are vapor-tensions, L_1 and L_2 latent heats of vaporization, λ the heat disengaged on mixing $n + n'$ molecules of two liquids, and T is the temperature. As is readily seen, this formula is a special adaptation of Kirchoff's formula; in reality, they may be considered as expressing similar relations.

Nernst[3] by carrying out a closed cycle in the thermodynamic

[1] Ueber einen Satz der Mechanischen Wärmetheorie und einige Anwendungen desselben: *Ann. der Phys. Pogg.*, **103**, 177, *1885*.

[2] *Loc. cit.*, 281.

[3] Theor. Chem., 102-105.

sense of the term, in which semi-permeable membranes play a conspicuous rôle, has arrived at this equation:

$$(C) \qquad Q_{(x)} = -RT^2 \frac{d}{dT}\left(ln \frac{p_0}{p} + x\, ln \frac{P_0}{P} \right)$$

in which $Q_{(x)}$ is the heat of mixture,—equal to the decrease of the internal energy,— R and T have the same signification as in formula (A), p_0 and P_0 are the vapor-tensions of the pure liquids, and p and P the vapor-tensions at the moment of mixing, and x the number of molecules of one component to one molecule of the other. As is evident, this formula is quite similar to that of Kirchoff, which, Nernst claims, is but a special case of his more general one.

Duhem[1] has, by the application of the thermodynamic potential, which has proven so fruitful in his hands, developed the following formulas, each of which is applicable to the heat evolved or absorbed when to a solution of two liquids, certain masses of either liquid, δM_1 or δM_2 are added:

$$(D) \qquad EL_1 = \frac{4\Sigma R}{\alpha_1\, \omega_1} T^2 \frac{d}{dT} \log \frac{p_1\,(x, T)}{P_1\,(T)},$$

$$(D\text{ bis}) \qquad EL_2 = \frac{4\Sigma R}{\alpha_2\, \omega_2} T^2 \frac{d}{dT} \log \frac{p_2\,(x, T)}{P_2\,(T)};$$

in the formulas E is the mechanical equivalent of heat; L_1 and L_2 heats of solution; Σ the specific volume of hydrogen in normal conditions of temperature and pressure; R a constant having the same value for all ideal gases; α_1 and α_2 atomicities; ω_1 and ω_2 molecular masses, T the temperature; p_1 and p_2 the vapor-tensions of the solutions; and P_1 and P_2 the vapor-tensions of pure liquids. It is at once apparent that this equation, if Duhem's complete, but rather prolix manner of writing be suitably transformed, is identical with the one developed by Kirchoff.

An important conclusion can be drawn from the above equations, in case the heat of solution turns out to be equal to zero; then, $\frac{d}{dT} \log \frac{p'}{p}$ becomes equal to zero too, and the ratio $\frac{p'}{p}$ is independent of the temperature. That, in reality, to a very close

[1] Dissolutions et Mélanges; Troisiéme Mémoire; Les Mélanges Doubles: Travaux et Mémoires des Facultés de Lille, 100, *1894*.

approximation such is the condition of affairs for certain dilute solutions has been known since 1857; and such solutions are said to follow the law of von Babo,[1] which says that the heat of dilution must be zero.

Now we have found that the mixtures of the first class at least, that is, those made up of benzene, toluene, monochlor- and monobrombenzene, have vapor-tensions which are practically independent of the temperature, that is, the fraction $\frac{p'}{p}$ has the same value for all temperatures. It follows then that no thermal change should accompany the act of mixing of the liquids; their heat of solution of dilution is zero. No experiments so far as I know, which can give evidence as to the correctness of this statement, have been performed; but there can be no questioning of the truth of the relation developed and it is not at all probable that the determinations of the vapor-tensions are much in error.

In order to put this prevision of theory to the test of experience, I have made a number of determinations of the thermal effect of mixing liquids, especially those of the first class. Two methods were employed, that requiring the use of a Bunsen's ice-calorimeter, and that depending upon the measurement of the change of temperature.

The ice-calorimeter which was employed was of comparatively large size, the inner tube having an internal bore of twenty mm., and a length of 200 mm. within the outer tube. The calorimeter was filled, set up, and manipulated nearly as recommended by Schuler and Wartha, the amount of mercury absorbed or expelled being weighed.

After the calorimeter had been gotten into normal working condition, it was found that a continuous formation of ice was occurring around the inner tube. The amount was, however, not only slight, but also very constant, so that it was possible to apply an entirely reliable correction for it.

The cooling of the liquids to o° and their subsequent mixing was accomplished in the following manner: A thin glass tube closed at one end and of such internal diameter as to permit of

[1] Berichte über die Verhandlungen der Gesellschaft für Beforderung der Naturwisseuschaften au Freiburg in Brisgau. January, 1 57, 282.

its being easily but snugly slipped into the inner tube of the calorimeter was of such length that about an inch of it projected out of the calorimeter. A cylindrical pipette, fitting easily into the glass tube just described, had its lower orifice directly below the bulb, and was closed by means of a glass rod running axially up through the pipette and ground accurately into the orifice; a bit of rubber tubing was slipped over the glass rod, which could be pushed down between the rod and the stem of the pipette, thus closing the latter above. The pipette was held in place in the tube by means of a tightly fitting cork.

A piece of aluminum foil was for about two-thirds of its length cut into in several places along each side nearly to the middle, and the parts thus formed were so bent that, when the other third of the foil was rolled into cylindrical shape and slipped over the lower part of the bulb of the pipette, where it was held by its own elasticity, they formed a number of small paddles, those on one side directed upwards, those on the other directed downwards. Such a stirrer permits of a rapid and complete mixing of liquids.

To make a determination, a certain amount of one liquid is introduced into the pipette and weighed therein. The other liquid is weighed in the tube which is provided provisionally with a cork. The aluminum stirring contrivance is then slipped over the bulb of the pipette, and the latter passed into the tube, being held in place by a tightly fitting cork; the pipette is not pushed deep enough into the tube to have its orifice dip in the mixture of liquids, and the paddles reach to the bottom of the tube. A weighed dish of mercury is allowed to catch the expelled mercury of the empty calorimeter for exactly half an hour before the liquids are introduced; by this means the calorimeter correction just before the determination is obtained. After the introduction of the tube and pipette, the calorimeter is allowed for a half hour or so to get again into its normal state. After this has come to pass, a fresh dish of mercury is put under the mercury tube, the cork holding the pipette is lifted, the glass rod is raised a little, and the liquid in the pipette allowed to run out. The pipette is then tightly closed, and twisted around for a half minute or so to thoroughly mix the two liquids. The cork is

again inserted in the tube, and the whole left for exactly half an hour. At the expiration of that time, the mercury vessels are changed, and the calorimeter left to itself for another half hour, when the mercury vessels are again changed, and the tube and pipette removed. The pipette is again weighed, and the difference between the two weights gives the amount of liquid. The amount of mercury expelled from the apparatus during the last half hour should, if the thermal equilibrium, disturbed by the heat evolved or absorbed by the mixture of the liquids, has reestablished itself, and if no change in the velocity of the freezing of the water itself has supervened, be equal to the amount expelled in the first half hour; in other words, the corrections in each case should be equal. This I found to be invariably the case. The heat effect of the mixing of the liquids is accordingly to be obtained from the excess or deficit of the amount of mercury expelled or absorbed in the next to the last half hour compared with that expelled during the first and the last half hours. This difference divided by 0.01544 gives the number of lesser calories measuring the heat effect of the mixing of the liquids.

By a most scrupulous attention to details in manipulation and to observance of time, as well as to care in weighing, I think that the determinations are exact to one-tenth calorie, and even to less than that.

I give in the following experiments the data obtained in the determination of the thermal effect of mixing such liquids as have been found in the foregoing pages to show the simplest behavior, and have hence been grouped into the first class. The negative sign before a datum is indicative of an absorption of heat, and consequent formation of ice and expulsion of mercury, while the positive sign indicates an evolution of heat etc.

Experiment 1.—Heat effect of mixing chlorbenzene and toluene:

Chlorbenzene	3.0028 grams.
Toluene	4.3032 "
Calorimeter correction in weight of mercury	—0.0013 "
Weight of mercury moved	—0.0018 "
" " " " due to mixing of liquids	—0.0005 "
Thermal effect measured in lesser calories	—0.032 "

Experiment 2.—Heat effect of mixing chlorbenzene and toluene:

Chlorbenzene	3.7715 grams.
Toluene	4.2190 "
Calorimeter correction in weight of mercury	—0.0014 "
Weight of mercury moved	—0.0020 "
" " " " due to mixing of liquids	—0.0006 "
Thermal effect measured in lesser calories	—0.033 "

Experiment 3.—Heat effect of mixing brombenzene and toluene:

Brombenzene	4.9530 grams.
Toluene	4.3680 "
Calorimeter correction in weight of mercury	—0.0009 "
Weight of mercury moved	—0.0020 "
" " " " due to mixing of liquids	—0.0011 "
Thermal effect measured in lesser calories	—0.072 "

Experiment 4.—Heat effect of mixing brombenzene and toluene:

Brombenzene	1.1611 grams.
Toluene	7.3887 "
Calorimeter correction in weight of mercury	—0.0010 "
Weight of mercury moved	—0.0005 "
" " " " due to mixing of liquids	+0.0005 "
Thermal effect measured in lesser calories	+0.032 "

Inasmuch as benzene solidifies at a temperature somewhat above that of melting ice, was not possible to carry out determinations in the ice-calorimeter with it in the pure state; accordingly I prepared a mixture containing 97.37 per cent. benzene and 2.63 per cent. chlorbenzene, which was used in experiment five.

Experiment 5.—Heat effect of mixing benzene and chlorbenzene:

Mixture of benzene and chlorbenzene	3.0208 grams.
Chlorbenzene	6.3470 "
Calorimeter correction in weight of mercury	—0.0013 "
Weight of mercury moved	—0.0030 "
" " " " due to mixing of liquids	—0.0017 "
Thermal effect measured in lesser calories	—0.101 "

An inspection of the above data shows that none of the heat effects is much above the limit of accuracy of which the method was judged capable. It was deemed worth while, however, to make some determinations of the heat effects brought about by

mixing liquids by means of thermometric measurements, especially for mixtures of benzene and other liquids, as benzene in the pure state could not be used in the ice-calorimeter. The apparatus used, although simple, is capable of telling with considerable accuracy whether there occurs a change in temperature when two liquids are mixed. It consisted of a large U tube, in one branch of which was fitted a thermometer graduated in hundredths of a degree, such as described by Beckmann,[1] and recommended for cryoscopic and ebullioscopic work, and in the other a pipette similar to the one described above in connection with the ice-calorimeter. The U tube had a very narrow side tube towards the top of one branch, which when stopped with cotton wool permitted the egress of air without any evaporation of the liquids in the large tube to speak of. The stirrer employed was similar to the one used with the pipette in the ice-calorimeter.

A weighed quantity of one liquid was put into the U tube, and a quantity of the other liquid was weighed in the pipette. The thermometer and pipette were put in the tube tightly by means of good corks, the whole apparatus supported on a retort stand, and wrapped snugly with a thick layer of cotton wool. The apparatus was then set in a room the temperature of which could be easily kept within twenty-five to thirty degrees C. for several hours. By working at this rather high temperature, the disturbing effect due to the proximity of the person of the operator was considerably lessened. When the apparatus had remained in the room for a couple of hours, the thermometer was read off at intervals of a minute for ten minutes, the contents of the pipette made to flow into the U tube, the two liquids were mixed as rapidly as possible by a twirling and up and down motion of the pipette, around which was clasped the aluminum stirrer, and then the temperature was read off at each minute for ten minutes longer. The pipette was then again weighed so as to get the actual amount of the liquid discharged by it, since it never occurred that it emptied itself completely.

The experiments carried out by means of this thermochemical apparatus limit themselves to mixtures of benzene with monochlorbenzene and with chloroform. They, together with those

[1] *Ztschr. phys. Chem.*, **2**, 644, *1888*.

carried out with the ice-calorimeter, are perhaps sufficient to serve as experimental corroboration of the theoretical relations between heat of solution and vapor-tension.

It is perhaps best to append the whole series of determinations in order that the reader may judge for himself of the accuracy of the results.

CHANGE OF TEMPERATURE ON MIXING FOUR GRAMS MONOCHLORBENZENE AND 26.524 GRAMS BENZENE.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	2.242°	11	2.339°
2	2.258°	12	2.348°
3	2.272°	13	2.369°
4	2.291°	14	2.381°
5	2.307°	15	2.388°
6	2.318°	16	2.390°
7	2.330°	17	2.396°
8	2.344°	18	2.394°
9	2.352°	19	2.388°
10	2.365°	20	2.380°

CHANGE OF TEMPERATURE ON MIXING 6.55 GRAMS MONOCHLORBENZENE AND 17.54 GRAMS BENZENE.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	2.591°	11	2.709°
2	2.603°	12	2.751°
3	2.618°	13	2.803°
4	2.622°	14	2.820°
5	2.630°	15	2.829°
6	2.638°	16	2.838°
7	2.641°	17	2.847°
8	2.649°	18	2.853°
9	2.651°	19	2.861°
10	2.655°	20	2.872°

CHANGE OF TEMPERATURE ON MIXING 10.86 GRAMS MONOCHLORBENZENE AND 7.31 GRAMS BENZENE.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	1.830°	11	1.421°
2	1.803°	12	1.400°
3	1.790°	13	1.395°
4	1.775°	14	1.372°
5	1.762°	15	1.370°
6	1.760°	16	1.420°
7	1.761°	17	1.435°
8	1.733°	18	1.450°
9	1.710°	19	1.445°
10	1.691°	20	1.438°

CHANGE OF TEMPERATURE ON MIXING 12.81 GRAMS CHLOROFORM AND 11.87 GRAMS BENZENE.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	1.489°	11	3.316°
2	1.520°	12	3.348°
3	1.531°	13	3.321°
4	1.540°	14	3.280°
5	1.561°	15	3.262°
6	1.573°	16	3.236°
7	1.582°	17	3.186°
8	1.608°	18	3.160°
9	1.621°	19	3.138°
10	1.632°	20	3.132°

It is apparent from these results that the change of temperature when benzene and monochlorbenzene are mixed does not exceed but a few hundreths of a degree, and even when the relative amounts of the liquids are about the same the change is in one case positive, in another negative, so that it is perhaps legitimate to judge that the change of temperature is largely due to the probability that the two liquids are at slightly different temperatures to begin with, and that in reality no or but an exceedingly slight heat effect occurs when these two liquids are mixed.

In the mixing of benzene and chloroform, however, there is a considerable rise of temperature, as indeed might be expected, since mixtures of chloroform and benzene do not in their vapor-tensions present the simplest phenomena. I have experimented with several other mixtures of liquids not belonging to the first class, especially with the ice-calorimetric method, and have found that they present certain abnormalities, some absorbing heat, and some evolving heat; these determinations, together with certain theoretical considerations, will form the substance of a subsequent paper.

Considering the above experiments as a whole, we may conclude that they are in entire corroboration of the formulas (A), (B), (C), and (D).

Nernst[1] found by the comparison of the theoretical conclusions with certain experimental data that the maximum of work, ob-

[1] Ueber die mit der Vermischung Konzentrirter Lösungen verbundene Aenderung der freien Energie: Sonderabdruck aus Nr. 12 der Nachrichten von de Königlichen gesellschaft der Wissenschaften zu Göttingen. v. J., 1892.

tainable by mixing two concentrated solutions with the same solvent, is "often" equal to the concurrent thermal change.

He then proposes to call "a homogeneous mixture of two substances, of which the maximum of work which can be obtained by a change of its composition, is measured by the concomitant thermal phenomena," an "ideal concentrated solution."

The contrast between "ideal dilute solutions" and "ideal concentrated solutions" is best shown by a consideration of the equation which rules over all Nature's happenings; this, according to Helmholtz,[1] is

$$F - Q = T\frac{\delta F}{\delta T}$$

wherein F represents the decrease in the "free energy" (freie Energie); Q that of the "total energy" (Gesamtenergie), and T the initial and final temperature, assumed to be the same in the operation under consideration. The characteristic of the "ideal dilute solutions" is that $Q = 0$ and that of the "ideal concentrated solutions" is that $F = Q$.

My object in mentioning these acute distinctions by Nernst is to call attention to the fact that there are certain combinations of substances (liquids) which, when mixed, develop no or very little heat, no matter what the relative proportions may be; that is, there exist "ideal dilute solutions" which may have any composition whatsoever, or, in other words, concentrated solutions may often follow the laws supposed to belong exclusively to dilute solutions. It is questionable, then, whether the notion of "ideal concentrated solutions" is necessary in science.

15. VAPOR-TENSIONS OF MIXTURES OF ACETIC ACID WITH BENZENE AND WITH TOLUENE.

Two series of determinations were carried out on the mixtures of benzene and acetic acid, one at 35° and one at 20°, but one, however, for the mixtures of toluene and acetic acid, at 35°. In order to apply to the experimental results of the work, our mode of calculation of the vapor-tensions, it is necessary to know the molecular mass of gaseous acetic acid at the above two temperatures. Now acetic acid even in the vaporous condition is

[1] Zur Thermodynamik chemischer Vorgange. Sitzungs-Berichte der Berliner Akedemie, 22, *1882*.

made up in part of polymerized molecules, so that it is not legitimate to set its molecular mass equal to that corresponding to the formula $C_2H_4O_2$. What the actual molecular mass of the gaseous acid at 35° and 20° is, can be easily calculated by the aid of the vapor-density determinations of Bineau[1] which are the more applicable to the case in hand as his vapor-density measurements were made under the same conditions as my vapor-tension determinations; that is to say, Bineau measured the amount of acetic acid that diffused into a definite volume of air at a fixed temperature. The molecular mass of acetic acid as deduced from Bineau's observations, is 104 for 35° and 110 for 20°. It may be worth while to remark that an error of five in the molecular mass will not entail an error of one millimeter in the vapor-tension: we may with all confidence then adopt the above molecular masses of acetic acid in state of vapor as quite accurate.

The necessary data of the experiments are given in tables XI to XIII, the superscription to each vertical column renders any explanation of them here superfluous.

TABLE XI.

Vapor-Tensions of Mixtures of Benzene and Acetic Acid at 35°.
Vapor-Tension of Benzene at 35° is 146 mm. of Mercury.
Vapor-Tension of Acetic Acid at 35° is 26.5 mm. of Mercury.

Per cent. of $C_2H_4O_2$ in liquid mixture.	Per cent of $C_2H_4O_2$ in gaseous mixture.	Grams $C_2H_4O_2$ in vapor.	Grams C_6H_6 in vapor.	Tension of $C_2H_4O_2$ in mm.	Tension of C_6H_6 in mm.	Volume of air in mm.	Barometer in mm.	Internal pressure in mm.
6.44	2.45	0.0461	1.3759	3.5	140.0	1955	758	14
15.17	4.74	0.0834	1.3580	6.4	129.2	1958	758	15
37.10	8.25	0.0700	1.5840	10.5	117.0	1020	767	16
43.99	11.02	0.0867	0.5243	13.2	106.5	1019	766	16
49.86	12.26	0.0931	0.4849	14.0	103.1	1020	766	17
53.24	13.33	0.0969	0.4731	14.9	97.6	1020	766	17
54.65	13.82	0.0990	0.4630	15.3	97.3	1020	766	17
56.60	14.62	0.1063	0.4677	16.4	96.0	1020	766	17
73.87	20.18	0.1156	0.4585	18.4	72.7	1019	766	16
80.00	26.91	0.1351	0.2751	22.3	59.3	1020	766	17

TABLE XII.

Vapor-Tensions of Mixtures of Benzene and Acetic Acid at 20°.
Vapor-Tension of Benzene at 20° is 75.6 mm. of Mercury.
Vapor-Tension of Acetic Acid at 20° is 11.7 mm. of Mercury.

[1] Recherches sur les Relations des Densités des Vapeur avec les Équivalents Chimiques: *Ann. chim. phys.*, **18**, 226, *1846*.

Per cent. of $C_2H_4O_2$ in liquid mixture.	Per cent. of $C_2H_4O_2$ in gaseous mixture.	Grams $C_2H_4O_2$ in vapor.	Grams C_6H_6 in vapor.	Tension of $C_2H_4O_2$ in mm.	Tension of C_6H_6 in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
53.24	11.99	0.0440	0.2291	6.6	48.7	1018	760	16
80.00	21.97	0.0576	0.2100	9.1	33.0	1018	760	16
97.28	64.66	0.0674	0.0276	11.4	6.2	1018	760	16

TABLE XIII.

Vapor-Tensions of Mixtures of Toluene and Acetic Acid at 35°.
Vapor-Tension of Toluene at 35° is 47.2 mm. of Mercury.
Vapor-Tension of Acetic Acid at 35° is 26.5 mm. of Mercury.

Per cent. of $C_2H_4O_2$ in liquid mixture.	Per cent. of $C_2H_4O_2$ in gaseous mixture.	Grams $C_2H_4O_2$ in vapor.	Grams C_7H_8 in vapor.	Tension of $C_2H_4O_2$ in mm.	Tension of C_7H_8 in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
49.00	32.66	0.0911	0.1661	15.0	31.8	1020	760	18
60.88	37.91	0.1025	0.1485	17.4	28.5	1020	760	18
83.37	56.36	0.1252	0.0858	22.2	16.7	1020	760	18

From the above data curves were constructed on a large scale with percentages of composition as abscissas and vapor-tensions as ordinates (one inch on the axis of abscissas corresponded to five per cent.; one inch on axis of ordinates to ten mm. of pressure); these proved to be perfectly regular, and passed directly through most of the points.

The points for acetic acid either fell upon or very close to the straight line connecting the left hand origin of the coordinate system with the point on the right hand axis of ordinates corresponding to the value of the vapor-tension of pure acetic acid at the temperature in question, *viz.*: 26.5 for 35°, and 11.7 for 20°, the acetic acid vapor-tension curve is simply a straight line, then, when the composition is expressed in percentages. An interesting conclusion to be drawn from this fact is that the partial tension of acetic acid is the same, be it mixed with benzene or with toluene; the specific influence of the diluting liquid seems to be extremely slight, if, indeed, there is any at all. This circumstance also indicates that the molecular condition of the acid is the same when it is dissolved in either of the hydrocarbons so as to form solutions of the same strength; this insight into the molecular structure of acetic acid enables us to determine by a little calculation its molecular mass not only in the dissolved but also in the pure state. In the following section will be set forth the *modus operandi*.

From the curves drawn as just described above, the partial pressures of the various constituents of the mixtures were taken for concentrations corresponding to ten, twenty, thirty, ... ninety per cent. of acetic acid; the data thus obtained are given in Table XIV.

TABLE XIV.

Partial Pressures of Benzene, Acetic Acid, and Toluene.

Per cent. of $C_2H_4O_2$ in liquid mixture.	Partial pressure of C_6H_6 at 35° in mm.	Partial pressure of $C_2H_4O_2$ at 35° in mm.	Partial pressure of C_7H_8 at 35° in mm.	Partial pressure of C_6H_6 at 20° in mm.	Partial pressure of $C_2H_4O_2$ at 20° in mm.
10	138.4	2.8	44.5	71.4	1.2
20	130.9	5.6	41.6	67.5	2.3
30	122.2	8.2	38.6	63.1	3.5
40	112.6	11.1	35.0	58.2	4.8
50	102.4	13.6	31.9	53.2	6.0
60	90.7	16.2	27.8	47.1	7.2
70	76.7	19.1	23.1	40.1	8.4
80	59.1	21.7	18.4	31.1	9.6
90	35.1	24.2	11.1	18.5	10.7

16. THE MOLECULAR MASS OF LIQUID ACETIC ACID AND A GENERAL METHOD OF DETERMINING MOLECULAR MASSES OF LIQUIDS.

The data given in the preceding section on the vapor-tensions of mixtures of acetic acid and benzene, taken in connection with the fact that the partial tension of benzene in its solutions is directly proportional to its concentration, permit of determining the molecular mass of the acid when diluted to any degree whatsoever with the hydrocarbon; and this special case may be generalized so as to permit of universal application. Furthermore, if the molecular mass of a substance be known in solutions of every degree of concentration, it is possible by a little extrapolation to pass over to the molecular mass of the pure liquid. It is, of course, assumed in making such an extrapolation that no break occurs in the continuity of the phenomenon, that is, the addition of very small quantities of a normal liquid to an associated one occasions correspondingly small changes in the degree of complexity of the molecules of the latter.

The way in which I have gone about to get at the molecular mass of acetic acid in benzene and toluene solution is as follows:

In a system of coordinates, molecular masses of acetic acid from 0 to 100 were laid off on the axis of abscissas (twenty inches

long), and on the axis of ordinates, the vapor-tensions were taken from 0 to 150 mm. of mercury (fifteen inches long). A straight line was drawn from the point 100 on the axis of abscissas and 0 on the right-hand axis of ordinates to the point 0 on the axis of abscissas and 146 (benzene at 35°), 75.6 (benzene at 20°), and 47.2 (toluene at 35°). Upon this straight line must lie all the points corresponding to the partial tensions of benzene or toluene dissolved in acetic acid. So points were marked along it giving the value of the partial tensions of benzene and toluene in solutions containing ten, twenty, thirty, etc., per cent. of acetic acid, the data being taken from table XIV.

The value of the abscissas which these points determine give the number of molecules of acetic acid contained in 100 molecules of the mixture. All that has to be done now is to solve for every case this problem: Given a mixture containing m parts of a liquid A, having a molecular mass z, and n parts of a liquid B, having a molecular mass y; the mixture is made up of r molecules of A, and s molecules of B. What is the value of x in the terms of y, m, n, r, and s?

In the case before us, we will take acetic acid for the liquid A, and benzene, or toluene as the case may be, for B; then n is equal to $(100-m)$, and s to $(100-r)$.

It is easily found that the solution of our problem is

$$x=\frac{m\,s\,y}{r\,n} \text{ or } x=\frac{m\,(100-r)\,y}{(100-m)\,r}.$$

In the accompanying tables, XV, XVI, and XVII, the values of m, r, and x, are given.

TABLE XV.

Molecular Mass of Acetic Acid dissolved in Benzene at 35°.

Percent. $C_2H_4O_2$ in liquid mixture.	Molecules $C_2H_4O_2$ in 100 molecules of liquid mixture.	Molecular mass of acetic acid.
10	5.2	158
20	10.6	164
30	16.6	167
40	23.1	173
50	30.0	182
60	37.7	193
70	47.2	203
80	59.3	213
90	75.6	227
100	100.0	240

TABLE XVI.

Molecular Mass of Acetic Acid dissolved in Benzene at 20°.

10	5.1	161
20	10.5	166
30	16.2	172
40	22.6	177
50	29.6	186
60	37.2	198
70	46.7	208
80	58.7	218
90	75.2	231
100	100.0	244

TABLE XVII.

Molecular Mass of Acetic Acid dissolved in Toluene at 35°.

Per cent. of $C_2H_4O_2$ in liquid mixture.	Molecules $C_2H_4O_2$ in 100 molecules of liquid mixture.	Molecular mass of acetic acid.
10	6.1	159
20	12.4	163
30	19.0	168
40	26.5	170
50	32.8	188
60	41.3	196
70	51.2	204
80	61.1	213
90	78.4	228
100	100.0	240

Considering tables XV and XVII first, we see that the values of x are approximately the same, the molecular mass of the acid becoming less and less as it is more and more diluted with benzene or toluene. It is remarkable that these two series of values for x fall out so nearly the same, for in the mixture of toluene and acetic acid, the differences of their vapor-tensions is so slight that the line of partial pressures of toluene is nearly horizontal, and an error of one millimeter in the determination of the partial pressure may occasion an error of four units in the molecular concentration; in the mixture of benzene and acid, however, the error arising from this source is not more than three-tenths of a unit, the angle made by the line of partial pressures being considerably greater than in the case of the other mixture.

For the determinations carried out at 20° on the mixture of benzene and acetic acid, it is seen that the number of molecules

long), and on the axis of ordinates, the vapor-tensions were taken from 0 to 150 mm. of mercury (fifteen inches long). A straight line was drawn from the point 100 on the axis of abscissas and 0 on the right-hand axis of ordinates to the point 0 on the axis of abscissas and 146 (benzene at 35°), 75.6 (benzene at 20°), and 47.2 (toluene at 35°). Upon this straight line must lie all the points corresponding to the partial tensions of benzene or toluene dissolved in acetic acid. So points were marked along it giving the value of the partial tensions of benzene and toluene in solutions containing ten, twenty, thirty, etc., per cent. of acetic acid, the data being taken from table XIV.

The value of the abscissas which these points determine give the number of molecules of acetic acid contained in 100 molecules of the mixture. All that has to be done now is to solve for every case this problem: Given a mixture containing m parts of a liquid A, having a molecular mass z, and n parts of a liquid B, having a molecular mass y; the mixture is made up of r molecules of A, and s molecules of B. What is the value of x in the terms of y, m, n, r, and s?

In the case before us, we will take acetic acid for the liquid A, and benzene, or toluene as the case may be, for B; then n is equal to $(100-m)$, and s to $(100-r)$.

It is easily found that the solution of our problem is

$$x=\frac{m\,s\,y}{r\,n} \text{ or } x=\frac{m\,(100-r)\,y}{(100-m)\,r}.$$

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20	12.4	163
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50	32.8	188
60	41.3	196
70	51.2	204
80	61.1	213
90	78.4	228
100	100.0	240

Considering tables XV and XVII first, we see that the values of x are approximately the same, the molecular mass of the acid becoming less and less as it is more and more diluted with benzene or toluene. It is remarkable that these two series of values for x fall out so nearly the same, for in the mixture of toluene and acetic acid, the differences of their vapor-tensions is so slight that the line of partial pressures of toluene is nearly horizontal, and an error of one millimeter in the determination of the partial pressure may occasion an error of four units in the molecular concentration; in the mixture of benzene and acid, however, the error arising from this source is not more than three-tenths of a unit, the angle made by the line of partial pressures being considerably greater than in the case of the other mixture.

For the determinations carried out at 20° on the mixture of benzene and acetic acid, it is seen that the number of molecules

of acid is less, and hence their molecular mass is greater, than when the determinations were carried out at 35°. This is just what is to be expected for the lowering of temperature has been found to be invariably accompanied by an increase in the condensation of the molecule.

I have sketched the curves corresponding to the values of m and x given in the foregoing tables, in a system of coordinates with percentage composition as axis of abscissas and molecular masses as axis of ordinates.

The curves for the mixture of acetic acid and benzene at 35° practically coincides with that of the mixture of acetic acid and toluene at 35°, while the curve for the mixture of benzene and acetic acid at 20° is parallel and slightly above the other two. The curves are perfectly regular in form, and if prolonged to cut the right-hand axis of ordinates cannot give values varying by more than one unit; accordingly it may be claimed that the point where the axis of ordinates is cut by the extrapolated curve gives to about one unit the molecular mass of acetic acid in the liquid state at the temperature taken for the determinations. The results of my extrapolations gives as the molecular mass of liquid acetic acid at 35°, 240, and, at 20°, 244.

It is interesting to compare these results with those obtained by Ramsay and Shields.[1] These investigators found by the determination of the superficial tension of acetic acid that its molecular mass between the temperature limits, 16° and 46°, was equal to 217.2 (60×3.62); although this result leaves room for considerable uncertainty as to what the molecular mass of the acid is at any given temperature between these limits, it is in corroboration of my results; for, as has been well established, the degree of association in the molecules of a complex liquid is greater the lower the temperature, and my results pertain to temperatures which are lower or about the same as the mean of the two extreme temperatures given by the two English chemists.

The method of determining the molecular masses of liquids described in this section is the only one as yet devised, which permits of the determination at any given temperature of the mass of the molecule.

[1] Ueber die Molekulargewichte der Flüssigkeiten. *Ztschr. phys. Chem.*, **12**, 470, *1893*.

It is founded on empirical results and depends upon no hypothesis other than the universally recognized one of Avogadro. It is applicable to all cases where the substances under examination can be accurately analyzed. It calls for no special apparatus, even a modest laboratory being provided with the necessary pieces. It requires no great amount of manipulative skill, and the results are obtained in relatively short time. I hope that it will be rigidly tested by chemists, and any omissions of this mere sketch be supplied.

RESUMÉ.

The main results of this article may be summed up as follows:

1. A method of determining the partial pressures of mixtures of liquids has been elaborated, and its sources of error discussed.

2. Although the method can be said to give the vapor-tensions of pure liquids with an accuracy equal to that obtainable by the best of other methods only when the liquids are not very volatile, the results obtained by it for mixtures of liquids of not too different volatilities are accurate enough to serve as the experimental basis for theoretical deductions and generalizations.

3. A number of mixtures of representative liquids have been investigated as regards their vapor-tensions.

4. In some cases, extremely simple relations were found; in others, certain complexities presented themselves.

5. A recalculation of Regnault's determinations of the vapor-tensions of some mixtures of normal liquids as well as a consideration of Raoult's conclusions and Brown's work on the boiling-points of solution showed that it was permissible to apply what was found true for any one temperature to any other.

6. The relations between the concentrations in the gaseous and liquid phases were found to be quite simple and entirely in accordance with the provisions of the theoretical relations established by Planck and Nernst.

7. The changes of temperature occurring when certain liquids were mixed were found to be very small, and the resulting mixtures were those which exhibited the simplest relations in their vapor-tensions.

8. The vapor-tensions of mixtures of acetic acid with benzene and with toluene were determined, and the results were such as

to permit of the determination of the molecular mass of the dissolved and liquid acid.

9. A general method for the determination of the molecular masses of associated liquids at any given temperature was developed and illustrated with acetic acid.

The experimental part of this investigation was done in a laboratory in the School of Mines at Paris, placed at my disposition by the authorities of that noble institution; and I here take the pleasant privilege of thanking them for the courtesy thus extended to me. My cordial thanks are also due to M. Emilio Damour, *Ingénieur civil des Mines*, for his foreseeing kindness in furnishing me with apparatus and material; especially are my thanks due, however, to M. H. LeChatelier, *Ingénieur en chef des Mines*, whose wise direction and good counsel have been of great value to me throughout the work.

CHICAGO, May 1, 1895.

WARNING AGAINST THE USE OF FLUORIFEROUS HYDROGEN PEROXIDE IN ESTIMATING TITANIUM.

BY W. F. HILLEBRAND.

Received May 29, 1895.

DUNNINGTON[1] has pointed out a source of error to be guarded against in estimating titanium in rocks and minerals by Weller's method, due, as he believes, to the partial reversion, in certain cases, of ordinary titanic to meta-titanic acid, which does not afford a yellow color with hydrogen peroxide. It remains for me to indicate another source of error in the possible presence of fluorine in the hydrogen peroxide.

For two years the colorimetric method has given reasonable satisfaction in this laboratory, but recently a new lot of hydrogen peroxide was purchased of a different brand from that hitherto used, and, after a time, it was noticed that the results obtained were in some instances far too high, and that no two determinations agreed.

It is known that hydrogen peroxide does not produce a yellow color in titanium solutions carrying hydrofluoric acid or fluorides, and moreover the addition of even a drop of the dilute acid to

[1] This Journal, 13, 210.

an already peroxidized titanium solution weakens the color. For this reason it is necessary to take the greatest care to insure the complete expulsion of all fluorine when dissolving rocks or minerals by means of hydrofluoric and sulphuric acids prior to the colorimetric estimation. A drop of hydrofluosilicic acid acts similarly, but the latter reagent cannot be made to completely discharge the color even if added in great excess.

This, however, was not suspected as the cause of our trouble until, on referring to the circular of one of the leading makers of hydrogen peroxide in this country, whose product has always given satisfactory results in titanium work, it was found that among the various acids enumerated as usually to be found in the commercial article, hydrofluoric acid appears. Talbot and Moody, in the *Technology Quarterly*, **5**, 123, mention hydrofluosilicic acid as of frequent accurrence in the peroxide manufactured a few years ago. On examining the suspected peroxide by neutralizing with fixed alkali, evaporating to dryness, and heating with strong sulphuric acid, fluorine was detected by the odor of the acid evolved and by its action on glass.

It is therefore imperative to use only hydrogen peroxide which if free from fluorine in estimating titanium, for its presence may utterly vitiate the results, even if only two or three cc. of the peroxide are employed.

LABORATORY OF THE U. S. GEOLOGICAL
SURVEY, WASHINGTON, D. C.

[FROM THE CHEMICAL LABORATORY OF THE LANDWIRTSCHAFTLICHEN-LANDES-LEHRANSTALDT IN CZERNOWITZ.]

THE VISCOSIMETRIC EXAMINATION OF BUTTER FOR FOREIGN FATS.

BY DR. NEWMANN WENDER.

Received July 1, 1895.

THROUGH a large number of investigations by Poisenille,[1] Girard, Hagenbach,[2] Graham, Rellstab, Pribram and Handl, Traube and Gartenmeister, to whose original investigations the reader is referred for the sake of brevity, it has been

[1] *Ann. der Phys. u Chem. Fogg.*, **58**, 424. *Ann. chim. phys.*, **64**, 129.
[2] *Ibid.*, **99**, 217.

established that a relation exists between the chemical composition of liquids and the velocity of transpiration just as there exists a relation between boiling-point and composition. There exists now a criterion for the purity of a substance, if a relation is found to exist between viscosity and boiling-point, at the same time, points of practical importance. From the investigations of Pribram and Handl it follows that observations of the specific viscosity or specific transmissibility of substances afford a hint as to the presence of adulterations and impurities, because these exert a decided influence upon the fluidity. The determination of the viscosity has found a practical value in the examination of oils and beer. The apparatus used for this purpose have been the viscometer of Engler and the septometer, both of which have found extended application. To these valuable, yet always expensive forms of apparatus, I have recently added the "Fluidometer," devised by me and manufactured by the firm of Max Kaehler and Martini, Berlin. I have communicated a description of the same to the Pharmaceutical Society of Berlin.[1] The apparatus possesses besides its inexpensiveness, other merits, chief among which is this, that by means of a simple compression bulb the liquid can be forced back and used for repeated determinations. The apparatus consists of a U formed capillary tube, both of whose limbs are enlarged and divided in such a manner that one arm holds ten cc. and the other two cc. liquid. According to the laws of communicating tubes the liquid flows from the wide limb through the capillary into the smaller limb, which is placed somewhat lower. The viscosity is calculated from the time which is required for the liquid to flow from the first division to the last upper division. There is no danger of error arising from evaporation or contamination with foreign substances in repeating the experiments, and, furthermore, the apparatus is easily and quickly cleaned.

According to the researches of Graham, in 1861,[2] confirmed by those of Pribram and Handl,[3] and by those of Gartenmeister,[4] it was found that the viscosity of a liquid increased with

[1] *Ber. d. Phys. Ges.*, Berlin, *1891*, 342.
[2] *Ann. Chem.* (Liebig), **123**, 90.
[3] *Loc. cit.*
[4] *Ztschr. phys. chem.*, **6**, 524.

the molecular weight, and the correctness of this law is evident from the following table:

	Pribram and Handl.						Gartenmeister.
Fatty acids.	Molecular weight.	Specific gravity at 20° C.	Boiling-point.	Specific viscosity at 10° C.	Specific viscosity at 30° C.	Specific viscosity at 50° C.	Absolute constant of friction at 20° C.
Propionic acid.....	74	0.9929	140.7	70.3	51.5	49.9	—0.1128
Butyric acid	88	0.9580	163.0	110.2	77.4	57.6	—0.1634
Valerianic acid.....	102	0.9386	184.0	152.4	103.3	71.5	—0.2279
Capronic acid.....	116	0.9279	199.7	222.2	139.7	97.8	—0.3263
Heptylic acid	130	0.9163	223.0	....	....	....	—0.4440
Octylic acid.....	144	0.9115	237.0	....	....	....	—0.5860
Nonylic acid.....	158	0.9053	253.0	....	....	....	—0.8480

Butter-fat differs from other animal fats in that it contains besides the glycerides of the higher fatty acids, a large amount of the glycerides of butyric, capronic, caprylic, and caprinic acids, and according to the investigations of Duclaux[1] the probable mean composition of butter-fat is:

Palmitin, stearin, olein, Traces of myristin butin	.....	91.5 per cent.
Butyrin	.....	4.2 "
Capronin	.....	2.5 "
Caprylin, caprinin, laurin (traces)	.....	1.8 "
		100.0

It appears therefore that mangarin consists of the glycerides of palmitic, stearic, and oleic acids only. If we compare the molecular weights of the constituents, it follows that the molecular weights of the glycerides of the higher fatty acids are much higher (806–890) than those of the glycerides in natural butter (302–470). The molecular weight determinations of Gaselli and Carcano[2] showed that the molecular weight of pure butter lies between 696–715 while that of margarin lies between 780–883. The fact that molecular weight stands in close relationship with viscosity was confirmed by Killing,[3] although it is known that

[1] Fleischman, Lehrbuch der Milchwirtschaft, Bremen, *1893*, 30.
[2] Centrbl. Agr. Chem., *1894*, 838.
[3] *Ztschr. Angew. Chem.*, *1894*, 643.

different samples of margarin show variable values, which could appreciably influence the results in the calculations.

Since it has been demonstrated by the work of Traube[1] that the relation between molecular weight and viscosity is not affected by solvents, I used in my "Fluidometer" a solution of the melted fat in chloroform, merely to avoid the difficult operation of maintaining the melting-point temperature of the fat and I did not lose sight of the fact that the viscosity of the solvent had to be taken into account. Chloroform was used, samples of which from different sources, required, in the mean, 20.04 seconds at 20° C. for efflux. The time of transmission of the solvent is set at 100 and the calculations for solutions are based upon this. From a large number of results I present the following average :

Viscosity value for pure butter	344.30	Time,	68.8
" " " margarin	373.20	"	77.4

Killings' investigations show further that with the one exception of cacao-fat, whose viscosity value falls below that of pure butter-fat, the values for vegetable fats, used by margarin manufacturers are decidedly higher.

Since, however, mixtures can be made whose values approximate that of butter-fat, the Reichert-Meissl method must be resorted to in order to detect the fraud.

A longer or shorter period of standing of the fat solution does not influence the result, whereas every degree of temperature above 20° C. decreases the time of efflux by 1.45 seconds. On the other hand, a decreasing temperature naturally has a retarding influence which averages 1.43 seconds for every degree. The determination of the exact amount of margarin added to butter when the amount of the former is small, cannot be expected of this method, but a largely adulterated sample is easily detected. From the above the following conclusions may be drawn :

1. The viscosity of butter-fat, in chloroform solution, as well as in the pure state, is always decidedly smaller than that of margarin or its solution of equal amount.

2. While the viscosities of different samples of butter show

[1] Berliner, Ber., *1886*, 871.

relatively small differences, samples of margarin from various sources, show much larger differences.

3. The viscosimetric determination can yield as good service in distinguishing butter-fat from margarin as any other physical method. The amount of margarin added to butter may also be approximately determined.

4. On account of its easy manipulation, its inexpensiveness, and the small amount of fat necessary, the "Fluidometer" is capable of yielding excellent results, not alone in the hands of experienced chemists, but likewise in those of government inspectors, etc.

THE EXAMINATION OF LARD FOR IMPURITIES.

By David Wesson.

Received June 22, 1895.

IN examining a sample of any material for impurities the analyst must first familiarize himself with the pure substance before he can detect wherein the sample under examination differs. If a definite compound is being dealt with, the problem is an easy one, but if we have an organic substance, which from the very nature of its origin is subject to many variations, the analyst is confronted with a problem of no small magnitude, and this is very true in regard to the accurate analysis of commercial lard, which is the fat rendered from various parts of the freshly slaughtered swine. Hogs being omniverous animals, it is reasonable to suppose that the fat will vary in accordance with the feed. It is a well-known fact that the lard from hogs which have been allowed to run in the woods and fatten on nuts of various sorts, preserves in a marked degree certain properties of the nut oils, and is much softer, containing more oil than that made from corn-fed hogs. That animals under proper conditions absorb food directly and deposit the same more or less unaltered in their tissues, seems to have been proven by experiments made some years ago at the Munich Physiological Institute.

That the fat varies greatly in different parts of the same animal has been demonstrated by various observers[1] as well as the writer.

[1] Wiley: Bulletin 13, Part IV, U. S. Dept. of Agr.; R. T. Thomson and H. Ballantyne; *J. Soc. Chem. Ind.* 9, 589, (590).

E. Spaeth[1] gives table of analytical data showing variations between back, kidney, and intestinal fat, taken from eight different hogs, of different ages. His results show considerable difference between the different animals.

The modes of rendering make considerable differences in the character of the fat. The comparatively low temperature used in kettle-rendering produces a fat of quite different analytical nature from that produced by treatment under high steam pressure in a closed rendering tank (*autoclave*). As most American lard is prepared by this latter method, this fact must be well borne in mind in interpreting analytical results.

Time is an important factor in determining the condition of a lard. A lard several months old will give analytical data which if compared with those of a fresh sample, would indicate adulteration.

The lard analyst who knows nothing of the history of a sample, and without such experience as will enable him to judge by the senses what sort of lard he is dealing with, is extremely liable to misinterpret analytical results and fall into grievous errors.

The methods used for the detection of cottonseed-oil in lard depend upon specific color reaction with different reagents, different physical properties of the fats, and the differences between the fluid portion ("olein") of the lard and that of the cotton oil.

Considering these tests in their order, we will first consider the reaction with silver nitrate, commonly known as the "*Bechi Test.*"

Cottonseed-oil when treated with an alcoholic solution of silver nitrate reduces the salt with formation of a brick-red or deep green color and deposition of metallic silver, while pure lard under like conditions should give little or no coloration and no metallic silver. The test has been applied in various ways by different chemists, but the writer has obtained the most satisfactory results by operating according to direction laid down by Dr. C. B. Dudley, in the Penn. R. R. specification for lard oil about six years ago. The solution used is made up with two grams silver nitrate, 200 cc. alcohol, and forty cc. ether. After expo-

[1] *Ztschr. Angew. Chem.* 1893, 133-136; also abstract in *Journal of the Society of Chemical Industry*, **12**, 608.

sure to sunlight, till reaction ceases, the solution is decanted or filtered into a dark bottle.

In testing, ten grams of melted lard and five cc. of the solution are well stirred together on the water-bath at 100° C. for fifteen minutes, at the end of which time most of the alcohol will have passed off. With pure lard there should be no coloration, while in the presence of cottonseed-oil the depth of color varies according to the amount and character of the oil, and a metallic mirror is deposited on the surface of the liquid fat.

Applying the test, in the manner described, to samples of steam lard known to be pure, and representing many thousand tierces, the writer found that more or less coloration of a purple tint was the rule rather than the exception. Believing that this apparent reduction was due to organic matter of a reducing nature held in the lard as a result of the process of rendering, the experiment was tried of washing the lard with a two per cent. solution of nitric acid. For this purpose about fifty grams of melted lard in a flask are shaken up with twenty-five cc. of the diluted acid, and after allowing to settle on the water- or steam-bath, the acid water is removed and the lard washed once with fifty cc. of hot distilled water. After settling till clear, ten cc. of the lard are pipetted off and the test made as described. In nineteen cases out of twenty, pure steam lard after this treatment will give no reduction whatever or suspicion of reduction, the fat remaining colorless at the end of fifteen minutes, whereas the reducing matter of cotton oil being unaffected by this treatment would give an unmasked reaction with the silver nitrate. While in the majority of cases the above treatment is all that is necessary to remove accidental reducing matters, we occasionally meet lards which have been treated at very high temperature and for a long time, which show as a result a slightly higher than normal per cent of free acid (normal is four-tenths to one per cent) and contain decomposition products of the animal fiber which have a very strong reducing action on our silver solution. Such samples must be first washed with diluted caustic soda solution and distilled water, and afterward with the nitric acid, before any definite conclusion can be drawn from the results of applying the silver nitrate test.

The condemnation of a sample of lard which gives a coloration with silver nitrate, without first purifying the fat as indicated, would be as absurd as it would be unjust, yet many good analysts have been known to do this very thing.

Dr. Ernest Millau applies the silver nitrate to the freshly separated fatty acids, but insists most forcibly on a preliminary preparation of the fat for analysis by a purification somewhat similar to the one outlined above. (See pamphlet[1] published by Ministero de L'Agriculture.)

Exception is taken to the silver nitrate test by various writers because of the misleading reaction obtained with lard improperly prepared for analysis, and also because cotton oil can be refined with oxidizing agents and the use of very high temperatures in such a measure as to destroy the specific reducing agent. Also very old oil will sometimes refuse to give any reduction. If such an oil were mixed with lard, it goes without saying that no reduction would not necessarily indicate pure lard, but the writer can say, as a result of several years' experience, that he has never run across any sample of oil failing to give the reaction which would be suitable to use in the preparation of an edible fat. If a lard containing cotton oil should become so old that the oil should lose its reducing power, the lard would be fit only for the soap-kettle.

The preponderance of evidence seems to be in favor of the silver nitrate test as being the best single test which has yet been brought forward for the detection of cotton oil in lard. When properly applied it is the most reliable for detecting small quantities.

The phosphomolybdic acid test, otherwise known as the Welmans test, first described in the *Pharm. Zeit.*, *1891*, **36,** 798, has been highly recommended by several writers, of late, as of value for the detection of vegetable oils in lard. Among them may be mentioned Rupp, Wimmer, Mansfield, and Goske, while H. Schweitzer and E. Lungwitz[2] state that they have found the test one of great value.

[1] Analyse Chemique des Matieres Grosses Agricoles, pas Ernest Millau, Directeur de Laboratoire d'Essais Technique de Marseilles.

[2] *J. Soc. Chem. Ind.*, 614, *June 1894.*

J. Lewkowitsch[1] says as the results of a series of careful experiments: "Welman's reaction can therefore be admitted as a preliminary test, the indications of which may, in some cases, give valuable hints as to the direction in which the examination of a sample has to be carried out and may serve as a useful corroboration of results obtained by other methods."

Samelson[2] concludes that the test is of no value and that the iodine figure is the only reliable test for the detection of cottonseed oil in lard. He bases the assumption on the fact that he found six samples of American lard with iodine numbers of 64.7 to 67.2, which were higher than any he had ever found recorded, whence he concluded that cotton oil must be present though not shown by the test.

George F. Tennille[3] publishes a very exhaustive paper on this test, and concludes that "the phosphomolybdic test may be considered to be of slight analytical value, and certainly does not fill that long-felt want of a simple test which will reliably indicate small percentages of cotton seed or other vegetable oils in lards." The writer has tried the test and arrived at the same conclusions.

Sulphuric Acid Test.—The color produced by the action of sulphuric acid on cottonseed-oil in a mixture with lard is often a good qualitative indication, but it so frequently happens that pure lards prepared under certain conditions will give similar coloration, that results must be taken with extreme caution, and in many cases had better not be taken at all.

Dr. J. Lewkowitsch[4] concludes: "The sulphuric acid color test may therefore only be used for purposes of preliminary information, and even then its indications should be interpreted with the greatest caution."

PHYSICAL TESTS.

Specific Gravity.—Lard freshly rendered in the writer's laboratory showed at $\frac{99^\circ}{15^\circ}$ C. a specific gravity of 0.8600 to 0.8610, while old samples of known purity have been observed running as high as 0.8620, while we have on record one specimen which

[1] *J. Soc. Chem. Ind.*, 617, *June 1894.*

[2] *Ztschr. anal. Chem.*, 189, *1894.*

[3] This Journal, 17, 33.

[4] Contributions to the Analysis of Fats, IV, Color Reaction, *J. Soc. Chem. Ind.*, 617, *June, 1894.*

ran as high as 0.8640, and gave no indication of cotton oil by other tests. The lard was nearly a year old and had been stored in tierces. Cottonseed-oil shows under like conditions 0.8683. With fresh lard as a standard we would have a difference between lard and cotton oil of 0.0083. The lard cited would therefore show $\frac{0.0040}{0.0083}$ or forty-eight per cent. of cotton oil, which shows the test to give preposterous results when working on old lards. It is of use in obtaining the proportionate components of a mixture when the specific gravities of the identical fats used in preparing the mixture are known.

Refraction Index.—As this depends to a great extent on the relative amounts of olein and stearin and palmitin present, it is quite evident that two samples of lard containing these ingredients in different proportions would show different indices. Wiley has published a large number of refraction indices in Part IV, Bulletin 13, Dept. of Agriculture, 1889, Lard and its adulterations. In table 18, he gives the results of analysis of six samples of Prime Steam lard drawn by C. H. Mixer, the official inspector of the board of trade in Chicago, and accompanied by his affidavit. The lards were of unquestioned purity yet their indices varied from 1.4911 to 1.4675, which shows that the refraction index is little better than specific gravity as a test *per se*.

Melting-point.—Any one who has experimented much with the melting-points of lard and lard compounds will, it is believed, readily agree that no suitable method has yet been proposed which will give analytical indications of any value except in cases of large admixtures of beef fat. This determination depends so largely on the manner of cooling the fat and the time elapsing after the cooling that it is of no value whatever as an indication of small adulteration.

Crystallizing-point of the Neutral Fat.—The observation of the manner of crystallizing on cooling of the melted fat gives valuable indication regarding the presence of beef fat.

H. Schweitzer and E. Lungwitz,[1] give their mode of procedure and results obtained with it. They rely on the test to a

[1] Commercial Analysis of Lard, *J. Soc. Chem. Ind.*, June, *1894*, 614, and July, *1894*, 709.

considerable extent for the detection of beef fat. Amthor and Zink[1] use this method among others.

The writer has derived very useful indications respecting the proportion of beef fat present in a mixture, by working in a somewhat different manner. As a rule pure lards chill below 30° before showing turbidity, while if beef fat is present crystallization begins at higher temperatures according to the amount present. A lard containing ten per cent. of beef stearin will cloud at a higher temperature than pure lard stearin.

Microscopical examination of the fat crystals deposited from ether is of value for the identification of beef fat when present in large enough amount. When only small amounts of oleostearine are present the test is not as conclusive as the cooling test, unless recrystallization is resorted to.

Crystallization-point of the Fatty Acids.— This method, first proposed by Dalican, has for a long time been considered a valuable criterion and is a very useful factor in passing upon the purity of a lard.

The crystallization-point depends upon the relative amounts of solid and fluid acids present, being higher of course in proportion to the increase in the former, but unfortunately the thermometer readings are not in exact ratio to the amounts added.

As the relative amounts of the fluid and solid acids vary in different parts of the same animal it is quite evident that pure lards will show quite different points of crystallization, according to the portion of the animal from which they have been prepared, and also according to the individual, as shown by the results on lards rendered in the U. S. Agricultural Laboratory in Washington and in the writer's laboratory in Chicago some years since.

Part of hog.	According to Wiley.	According to Wesson.
Head	36.6	35.4
Intestine	42.7	41.2
Leaf	41.3	41.5
Back and sides	...	39.7
Belly	...	39.7
Foot[2]	32.1	...

[1] *Ztschr. Anal. Chem., 1892*, 584 to 537.

[2] This sample was prepared by a packer but well authenticated.

The crystallization-point of Prime Steam lard or the lard of commerce, varies from 35.5 to 38. The majority of receipts during the past year have shown an average to 36.5, which would indicate that more of the softer parts of the hog are now used than formerly, when the average was one degree higher.

Lard oil has a crystallization-point of 31°–32°, while well pressed lard stearin should show not less than 43.5°.

Considering the wide range in crystallization-point of pure lard, we can only regard the test as a corroborative one, and useful in connection with others in passing upon the purity of a lard, but of little value in proving presence of small amounts of either cotton oil or beef fat.

IODINE ABSORPTION.

As the amount of iodine absorbed by a fat depends upon the chemical nature and quantity of the fluid acids present it is evident that in the case of lards it is impossible to draw sharp conclusions, for the softer the lard the more iodine absorbed and conversely. If a standard for purity of lard should be established saying that the correct absorption should be a certain figure, there would be little trouble for the adulterator to make a mixture of cotton oil and beef fat which would fully meet the requirements, and thus make the iodine number prove nothing so far as purity of a lard is concerned. An example or two will make this apparent.

	Iodine number.		
Cotton oil	108	10 parts.	10.80
Oleostearin	21	10 "	2.10
Steam lard	64.5	80 "	51.80
Mixture has iodine number			64.50

and contains twenty per cent. of adulteration. The number 64.5 is very near the average for Prime Steam lard and well within limits. Another case would be that of a mixture of intestinal lard testing 52 and cottonseed-oil testing 108, which would contain twenty-five per cent. of the latter and still test 65, while with twenty per cent. cotton-oil the sample would have an absorption of but 63.

In our first example the Dalican temperature of crystallization would be raised a little above normal by the oleostearin, while

in the second instance it would be about normal for pure lard. By normal we mean the temperature of crystallization corresponding to the amount of fluid acid indicated by the iodine number.

Besides the variations caused by the fat being taken from different parts of the hog, we have the difference in individual animals, caused by difference in feed. For instance, Wiley,[1] found on testing the lard rendered in his laboratory from different parts of the same animal, figures which differ considerably from the writer's, as shown in the following table:

	Wiley.		Wesson.	
Portions of animal.	Iodine No.	Point of crystallization.	Iodine No.	Point of crystallization.
Head	85.03	36.6	60.35	35.4
Intestine	57.34	42.7	52.14	41.2
Leaf	62.55	41.3	56.88	41.5
Back and sides			57.41	39.7
Belly			58.82	37.7

The results would seem to indicate that one of these hogs judged by the others must have been sadly adulterated. In the writer's opinion, the animal operated on by Wiley, which was purchased in Washington, was very likely one which had gathered a portion of its adipose in the woods of Virginia and adulterated its fat with the oils from beechnuts and acorns, while the writer's hog was a plain, every day Western corn-fed specimen, such as generally comes to the Chicago packers.

The crystallization-points would certainly indicate that considerable differences in the character of the oleins must be the cause of the great differences in the iodine numbers.

To observe the effects of age on samples, those of the writer cited above were tested again after three months standing in the laboratory at from 20° to 30° C., with the following results:

Head	63.64
Intestine	58.05
Leaf	61.02
Back and sides	60.50
Belly	63.95

Comparing these figures with those obtained on the fresh samples, which, if considered a standard of purity, would lead us to the conclusion that time had been adding some cotton oil. In

[1] Lard and Adulteration Bulletin 13, Pt. IV, U. S. Dept. of Agriculture.

the case of the leaf lard the quantity would appear to be eight per cent.

That age acts in a similar manner on steam rendered lard we can see no reason to doubt.

As a rule the iodine numbers of steam lards run considerably higher than most of the published results on lards.

The iodine numbers of prime steam lard range as follows:

Sample.	Crystallization-point.	Iodine number.	Remarks.
5662	39.30	61.95	Wiley: Lard and Adulterations; samples drawn and sworn to by C. H. Mixer, the official inspector at Chicago.
5663	38.05	63.82	
5664	....	60.34	
5665	....	65.12	
5666	39.10	60.85	

Sample.	Crystallization-point.	Iodine number.	Remarks.
1	36.3	67.22	Lard from 400 tierces and different packers. Age of samples, six to twelve months. All samples prime merchantable lard, and unquestionably pure. Tests made in our laboratory.
2	36.0	65.25	
3	36.3	69.06	
4	36.5	69.26	
5	35.6	67.30	
6	37.0	65.31	
7	37.3	64.31	
8	35.0	68.48	

L. E. Spaeth[1] gives results on fats from different parts of eight different hogs and draws the conclusion that a lard must not be considered adulterated merely because its iodine number surpasses sixty. Spaeth's results are:

Age of hog.	Iodine number of fat from Back.	Kidney.	Intestines.
Two years	63.25	61.15	62.90
Six to eight months	62.95	49.35	57.25
Ten months	55.50	55.88	50.60
Six months	60.10	55.80	52.30
Five to six months	57.08	50.20	51.75
Six to seven months	63.61	52.35	49.85
Ten months	60.95	46.60	47.60
Six to seven months	61.20	51.50	52.85
Mean	60.58	52.60	53.10

The above results are especially instructive as showing the great difference which exists between different animals as well as different parts of the same animal.

[1] *Ztschr. Angew. Chem.* 1893, 133-136.

As commercial lard is nowadays made largely from heads, back, and side fat, it is easy to account for the high iodine absorption of prime steam lards.

Iodine Number of the Fluid Acids.

As the fluid acids are the portion of the fat which absorb the iodine, and as the amount of fluid acids present in the fat determine its absorption, which also varies with the nature of the fluid acids present, it follows that the truly scientific method of analyzing a lard is to first determine the percentage of fluid acids present, and then from the iodine number of the fluid acids calculate the proportion of lard and cotton oil present.

This system of analysis was first published by Muter.[1] His process consists in precipitating the lead salts from a neutral solution, extracting the oleate with ether, decomposing the lead soap in the solution with dilute acid, determining the amount of oleic acid present by titrating a measured portion with standard alkali, and then determining the iodine number, using half a gram of the fluid acids under standard conditions. The process though tedious, gives very satisfactory results. Messrs. Muter and DeKoningh published some of the results of the process in the *Analyst, Feb. 1890*. They obtain for the fluid acids of tallow, 90; for lard, 93–94; while for cotton oil, 135.

N. J. Lane[2] reviews Dr. Muter's method, and describes an improvement which gives the results in much shorter time. His results, which were obtained in our laboratory, were as follows:

	Fluid Acids. Per cent.	Iodine number of same.	Hübl number of fat.	Saponification equivalent.	Crystallization-point of fatty acids.
Cottonseed stearin	68.05	141.09	99.3	288.21	36.6
Summer yellow cotton oil	75.16	141.96	108.36	397.51	32.4
Winter yellow cotton oil..	77.64	143.49	110.96	296.27	30.4
Cotton oil, Columbia, S. C.	76.73	141.97	108.95	284.75	33.8
Cotton oil, New Orleans..	76.67	140.59	109.23	288.94	33.4
Steam lard, ave'ge sample	64.15	99.48	64.96	287.85	37.4
Corn oil (maize oil).....	83.97	144.40	121.7	.....	....
Arachide oil.....	79.84	114.00	93.55	.....	....

In studying the above table it will be noted in the case of cot-

[1] *Analyst 1889.*

[2] This JOURNAL, 15, 110.

ton oil, that whatever variation there may be in the other constants, the iodine number of the fluid acids shows comparatively little variation.

The sample of steam lard mentioned was a composite sample of a number of lots of known purity, representing the article as made at that time.

Wallenstein and Finck[1] work with a modification of the Muter method, which guards more fully against oxidation of the fluid acids by contact with air.

They say: "In deciding qualitatively as to the purity of a fat it may be assumed that below the limit of ninety-six (iodine number of fluid acids) there is no admixture of vegetable oil (except it be cocoanut oil, which is however revealed by the saponification number of the sample). *Between ninety-six and 105 much depends on the origin of the fat.* For instance, Central European lards show ninety-three to ninety-six, while American lards vary between 103 and 106, and additional confirmation by Welman's or Bechi's test will be required to form a decisive opinion."

Results obtained are as follows:

	Iodine number of fluid fatty acids.	Iodine number of Glycerides.
Berlin ox tallow	92.2	38.3
Australian tallow	92.4	45.2
Hungarian mutton tallow	92.7	38.6
American western steam lard	104.5	65.4
Berlin hogs' lard	96.6	52.7
Hungarian hogs' fat	96.2	60.4
Viennese hogs' fat	95.2	60.9
Roumanian hogs' fat	96.0	59.5
White American cottonseed-oil	147.5	108.0
Yellow American cottonseed-oil	147.3	107.8
Yellow Egyptian cottonseed-oil	148.2	108.0
White English cottonseed-oil	146.8	106.5
White German cottonseed-oil	147.1	107.1
Yellow Peruvian cottonseed-oil	147.8	106.8
Maize oil	140.7	122.0
Arachis oil	128.5	98.5

The above results agree fairly well with Lane's, and are another contribution to the variation of hog fats. The authors attribute the high iodine absorption of the American lard to the

[1] *Chem. Ztg.* **12**, 1189-1191; also *J. Soc. Chem. Ind.* Jan. 31, *1895*, 78.

difference in feeding methods pursued in America and Europe. They are no doubt right, though the mode of rendering also differs.

At the present time the writer is aware of no method of analysis approaching the modified method of Muter for accuracy, and invariably applies it in doubtful cases.

G. Halphen[1] gives results of a method of separating the fluid and solid fatty acids based on difference in solubility of zinc salts in carbon bisulphide. Their results show that very imperfect separations are obtained and the process has little practical utility. The writer tried the same method in 1888, using gasoline, and obtained better but not satisfactory results.

In conclusion, I would say that working with the best analytical methods at our command, unless the origin of samples is known, the analyst is frequently at a loss to interpret results, in much the same manner as in passing upon a potable water of unknown history, and often when we see the self-confident manner in which small percentages of cotton oil are announced on very questionable data, we feel like exclaiming with the poet,

"Fools rush in where angels fear to tread."

March 12, 1895.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. NO. 7.]

THE ACTION OF HALOID ACIDS IN GAS FORM UPON THE SALTS OF ELEMENTS OF GROUP V OF THE PERIODIC SYSTEM.

BY EDGAR F. SMITH AND FRED. L. MEYER.

Received May 3, 1895.

AFTER observing the conduct of salts of the acids of elements of Group V toward hydrochloric acid gas, it was but natural that we should, with some interest, note the results arising when the other haloid acids, in gas form, were substituted for hydrogen chloride. It was useless to predict what might occur, and, therefore, the slight variations from preconceived notions were in no wise surprising. Taking up the study of the haloid acids and the various salts in the order of increasing molecular magnitude, we began with

[1] *J. de Pharm. et Chim.*, 30, 241-247, *1894*.

1. THE ACTION OF HYDROFLUORIC ACID GAS UPON SODIUM NITRATE.

The salt was exposed to the action of the gas in a platinum boat, carried in an iron tube. The temperature at which the reaction was conducted did not exceed 250° C. Not more than twenty minutes were allowed, or required, for the change which, from the analytical result given below, is evidently complete.

Experiment.—0.1052 gram of sodium nitrate gave 0.0530 gram of sodium fluoride, instead of 0.0520 gram, the theoretical amount.

A second trial gave a similar quantitative result.

2. THE ACTION OF HYDROFLUORIC ACID UPON PHOSPHATES.

The gaseous acid expelled nothing from sodium pyrophosphate. The boat contents sustained no less in weight. The water in the receiver gave no evidence of the presence of phosphorus when tested for it.

3. HYDROFLUORIC ACID AND VANADATES.

Sodium vanadate, thoroughly dried, was heated to 250° C., for one-half hour in an atmosphere of the acid vapor. Vanadium was found both in the receiver and in the boat. Upon repeating the experiment, increasing the temperature, and continuing the action of the acid vapor through an hour, about one-half of the vanadic acid was volatilized.

4. HYDROFLUORIC ACID AND ARSENATES.

In these trials sodium pyroarsenate was heated to about 400° C., while exposed to a brisk current of the acid vapors.

Experiment 1.—0.1893 gram of sodium pyroarsenate was used. When the boat-contents were examined 0.0872 gram of the pyro-salt was found unvolatilized.

Experiment 2.—0.2015 gram was treated in the same manner, with practically the same result. The volatilization, therefore, of the arsenic compound must be considered as incomplete.

To summarize, nitrates are entirely converted into fluorides by the vapors of hydrofluoric acid; with vanadates and arsenates the conversion is incomplete, while phosphates remain intact.

1. HYDROBROMIC ACID AND NITRATES.

Apparently no change occurs when these compounds are brought together in the cold. When gently heated aqueous vapor and bromine appear. In the course of half an hour the conversion into bromide is finished.

Experiment.—0.1887 gram of sodium nitrate gave 0.2286 gram of sodium bromide, instead of the theoretical 0.2273 gram.

2. HYDROBROMIC ACID AND PHOSPHATES.

Not even traces of phosphoric acid were expelled on heating sodium pyrophosphate in an atmosphere of hydrobromic acid.

3. HYDROBROMIC ACID AND VANADATES.

Sodium vanadate was acted upon in the cold. It became brown in color, and when the temperature was raised to almost 300° C., vapors escaped and condensed to an oily, reddish liquid beyond the heated portion of the tube. By the continued action of the acid this liquid acquired a green color, and small, green-colored crystals appeared. After the lapse of half an hour the liquid had completely solidified to a mass of radiating needles, having a beautiful green color. Several analyses of this compound showed the presence of 59.40 per cent. bromine and 14.65 per cent. vanadium, which would closely approximate the formula $V_2O_3Br_2.3HBr.7H_2O$, requiring 58.91 per cent. bromine and 15.02 per cent. vanadium. That such an oxybromide is not improbable may be inferred from the fact that Ditte (*Comptes rendus*, **102,** 1310) prepared the compound $V_2O_3Br_2.2HBr.7H_2O$, by boiling vanadic oxide (V_2O_5) with hydrobromic acid. It required 53.51 per cent. bromine and 17.06 per cent. vanadium. The conversion into bromide was not complete.

4. HYDROBROMIC ACID AND ARSENATES.

Quite a distinct reaction was evident with pure, dry, sodium pyroarsenate even in the cold. The salt assumed a dark-grey color. When a gentle heat was applied to it vapors were expelled; these condensed in the anterior portion of the tube to a pale-yellow, oily liquid, soluble in water. The temperature at which the reaction was carried out did not exceed 300° C. The boat contained pure sodium bromide.

Experiment 1.—0.5440 gram of pyroarsenate gave 0.6335 gram of sodium bromide, instead of 0.6331 gram, the theoretical quantity.

Experiment 2.—0.4277 gram of pyrophosphate gave 0.4984 gram of sodium bromide, while theory requires 0.4981 gram.

With this complete, quantitative expulsion of arsenic, and the non-volatilization of phosphoric acid before us, we next proceeded to the separation of the two acids, both being present as sodium pyro-salts.

Experiment 3.—0.1572 gram of sodium pyroarsenate and 0.1897 gram of sodium pyrophosphate were mixed and gently heated in hydrobromic acid gas. The phosphate remaining in the boat, when determined and calculated into pyro-salt, equaled 0.1903 gram. As it was free from arsenic, we did not estimate the arsenic contained in the receiver.

Through both hydrobromic acid and hydrochloric acid vapors, acting upon a mixture of arsenates and phosphates, a separation of the two acids may be effected.

The succeeding experiments relate to the conduct of nitrates, arsenates, and phosphates toward hydriodic acid gas. This was prepared by dropping water upon a mixture of amorphous phosphorus and iodine. It was carefully dried before it came in contact with the salts.

I. HYDRIODIC ACID AND NITRATES.

Sodium nitrate was changed by the gas into iodide. One approximate result may be given:

0.1039 gram of sodium nitrate gave 0.1886 gram of sodium iodide, instead of the theoretical 0.1833 gram.

Not one experiment could be completed, since explosions of considerable violence invariably occurred. A dark sublimate, apparently iodine, appeared in the tube, and after the lapse of a quarter of an hour a flash of fire ran through the tube, accompanied by a loud report. Not succeeding in finding a method to prevent this, further work was abandoned. These explosions

were doubtless due to the production of some unstable derivative of nitrogen and iodine.

Phosphates were not altered by contact with hydriodic acid gas.

2. HYDRIODIC ACID AND ARSENATES.

Sodium pyroarsenate was employed. In the cold the acid gas produced a change. Thus, 0.1592 gram of pyro-salt gave 0.2672 gram of sodium iodide, instead of 0.2689 gram. The arsenic volatilized, determined, and calculated into pyro-salt gave 0.1583 gram instead of 0.1592 gram. As explosions occurred in all the trials made we concluded to abandon the study.

It may not be uninteresting to present a scheme of the elements, composing Group V of the periodic system,

Nitrogen	Phosphorus	Arsenic	Antimony	——	Bismuth
14	31	75	120	164?	208
	Vanadium	Columbium	Didymium		Tantalum
	51	94	142		182,

and briefly review their deportment so far as known, when acted upon by the gaseous haloids. Nitrogen is fully expelled by all of them from nitrates. Phosphorus, existing as phosphates, apparently is absolutely uninfluenced and remains unaltered in the salts with which experiments were tried. Arsenic is only partially volatilized from arsenates by hydrofluoric acid gas, but is completely removed by any one of the remaining haloid acids. Antimony is fully expelled from antimonates by hydrochloric acid gas. No experiments have been tried with bismuth. Hydrofluoric and hydrobromic acid gas volatilize vanadium in part, while its removal from sodium vanadate by hydrochloric acid gas is complete. We have no knowledge of the action of hydriodic acid. Columbium yields volatile products with both hydrochloric and hydrobromic acid vapors. Didymium has never been subjected to this treatment. Tantalum is but slightly affected by the vapors of hydrochloric acid, although it has long been known that both the oxide of columbium and that of tantalum are volatilized to a marked degree when heated with aqueous hydrofluoric acid.

UNIVERSITY OF PENNSYLVANIA.

SEPARATION OF SOLID AND LIQUID FATTY ACIDS.

By L. de Koningh.

Received June 3, 1895.

THE April number of this Journal (289–295) contains a criticism, by Twitchell, of some processes for the separation of solid and liquid fatty acids. Being joint author with Muter of the process referred to on page 290, I wish to make a few observations.

The author states that he carefully carried out Muter's instructions in all important details. I beg to differ from him. We work directly on the fat and not on the fatty acids isolated therefrom. We do not *boil* with ether to dissolve the lead oleate, and after having taken the trouble to expel the ether by means of a current of carbonic acid we do not undo any good this may have done by passing a current of air, but add the Hübl solution directly, as we know the weight of the oleic acid by a previous titration. I feel sure, however, that there is a deal of exaggeration about all this danger of oxidation.

The lead oleate is precipitated as a bulky semi-fused mass which soon solidifies, and if ever so sensitive to oxygen can only be affected very superficially. When dissolving in ether the flask is nearly filled and the little air remaining is practically expelled by ether vapor, so that the few cc. of oxygen left certainly cannot cause a great oxidation. Even on filtering, the air is not likely to act much on a liquid which is always in an active state of evaporation and consequently repels the air. I feel sure that lead stearate and palmitate are insoluble in ether; then when carrying out the separation from the oleate, there soon comes a time when the filtrate no longer colors with ammonium sulphide. The author's suggestion, that it may be more soluble in ether containing lead oleate, is not supported by my own experience. Then Muter and I have stated in the *Analyst*, **15**, 49, that the liquid acid from tallow gives practically the iodine figure of pure oleic acid. For lard acid we found, however, ninety-three to ninety-four per cent., and I am pleased to see Twitchell's confirmation of this figure.

As gold alloys containing too little silver cannot be parted by means of nitric acid, so the separation of lead oleate from lead stearate fails if too little of the former is present. I published, two years ago, a short article in the *Chem. News*, **66**, 259, dealing with this subject, and refer to the same.

ACETIC ACID IN VINEGAR.

By Albert R. Leeds.

Received May 21,, 1895.

RECENTLY, having occasion to determine the acetic acid in many samples of vinegar, I was surprised to find how vague and unsatisfactory are the directions relating to this simple matter in many text-books and manuals for public analysts.

One of the latter recommends that fifty cc. of vinegar should be used and the titration performed with soda, no particular strength or indicator being mentioned. Another, in general terms, calls attention to the fact that only approximate results can be obtained with soda, its acetate having a feeble alkaline reaction. The indicator, in the presence of which it so reacts, is not stated. Sutton's Volumetric Analysis calls attention to the necessity of substituting phenolphthalein for litmus, the acetates of the alkalies and alkaline earths having a perfectly neutral reaction to the former. He further adds that colored vinegars may be so titrated even when highly diluted.

Beginning with twenty-five cc., which I found at once to be much too large a quantity, and using seminormal acid soda as a convenient strength of alkali, I presently reduced the volume of vinegar to ten cc. and finally to five cc. When this was diluted with fifty cc. of water in a white porcelain dish, and phenolphthalein was used as indicator, the end reaction was satisfactory, except in the case of highly colored vinegars. In these it is not sharp. Nor can litmus paper or litmus solution be satisfactorily used with them. Litmus gives not only a lower reading, but lower by a very variable amount in different vinegars. Sixteen samples tested as above described gave percentages ranging from 2.63 per cent. to 5.65 per cent., with a mean of 4.49. A mixture made up of twenty-five cc. of each, gave 4.44 per cent. The color of these samples was white to dark brown.

According to Sutton, Pettenkoffer titrates vinegar with a known excess of baryta and estimates the excess with decinormal nitric or oxalic acid by the help of turmeric paper.

Thinking that baryta might give a sharper reaction, though not discerning any advantage in the use of decinormal oxalic or nitric acid, I used an approximately decinormal baryta solution with phenolphthalein and decinormal hydrochloric acid. The results agreed to 0.01 per cent. with those obtained with soda, and ordinarily the latter would be the more convenient and preferable reagent.

Sutton recommends as a process applicable in all cases and however dark the vinegar may be, the method of C. Mohr, which consists in adding to a known quantity of the vinegar a known excess of barium or calcium carbonate in fine powder. Pure calcium carbonate, he states, is preferable, as it dissolves more readily.

In his excellent manual on "Foods" page 518, Blyth adds: "If absolutely accurate determinations are required, it is best to add an excess of pure calcium carbonate to a known weight; the liquid is boiled, filtered, and the residual carbonate dissolved in slight excess of normal hydrochloric acid and titrated back with soda and cochineal. From the amount of carbonate thus found to have been unacted upon, the total acidity is calculated."

This process failed entirely in my hands; I took fifty cc. of the vinegar and added two and a half grams of pure precipitated calcium carbonate in fine powder. The flask was corked loosely and shaken many times each day during the course of six days, at the end of which time the contents were still acid. Also, the flask was gently heated at intervals some five to six hours in all. The acetic acid still remaining, after filtering off the calcium carbonate, amounted to nine-tenths per cent. The figure calculated from the residual carbonate corresponded to 3.64 per cent., or a total of 4.54 per cent. as against 4.44 per cent., found directly with soda.

Regarding the amount of vinegar as too large and the difficulty as probably due to the slowness with which a very dilute solution of acid decomposed the carbonate towards the end of the reaction, I then treated ten cc. with excess of carbonate for

two hours under a return-condenser. This was somewhat more successful, the liquid containing 0.72 per cent. and the figure calculated from the residual carbonate corresponded to 3.85 per cent.—a total of 4.57 per cent.

The true percentage being thus rendered very doubtful, I then had recourse to another recommended by Blyth. He states, page 517, that the strength may be accurately estimated by distilling 110 cc. until 100 cc. have been drawn over, *i. e.*, ten-elevenths." The 100 cc. will contain eighty per cent. of the entire acid present in the 110 cc., and may be titrated; or the specific gravity of the distillate may be taken and the strength found from the following table: "A trial by this method yielded a distillate with specific gravity of 1.055 at 15°, corresponding in the table given to 4.25 per cent.; in one trial, the distillate should by titration, 4.23 per cent., in another, 4.24. Assuming for reasons stated below, that the correct percentage was 4.43, these figures correspond to ninety-six per cent. of the acid instead of eighty.

The method of distillation was then varied in the following manner: Ten cc. were diluted with fifty cc. of water in a small retort the neck of which was inclined upward and then bent downward to join the condenser. The distillation was continued until about two cc. remained in the retort when another fifty cc. of water was added and the distillation repeated—in all four times. The distillates had a faint acetous, mingled with a pronounced hop-like odor, on adding silver nitrate they presently darkened and on standing threw down a black deposit. They contained:

1.	3.73	per cent.	of	acid,	equivalent	to	83.2	per cent.	of total.
2.	0.54	"	"	"	"	"	12.1	"	" "
3.	0.081	"	"	"	"	"	1.8	"	" "
4.	0.041	"	"	"	"	"	0.9	"	" "

During this long process I had obtained only 4.39 per cent. acid or ninety-nine per cent. of the total.

The distillation was repeated in the same manner, using ten cc. of vinegar and fifty cc. of water in three successive additions, but the vinegar had previously been strongly fortified with phosphoric acid. One trial gave 4.507 per cent. acid, another 4.514.

The distillates gave no reaction for chlorine, and possibly the high figure was due to the presence of a little acetate.

Finally, in order to get rid of the disturbing influence of the coloring mattersf the following method was adopted. Fifty cc. of vinegar with fifty cc., of water and a drop of phenolphthalein were titrated with decinormal baryta, the latter being added to three cc. in excess, and then followed by five cc. of decinormal sulphuric acid. Whether the precipitates were allowed to settle in the cold or with warming, appeared to make no difference in the results, the coloring-matters being carried down very nicely. In one trial the precipitate was filtered off and thoroughly washed before titrating back with acid : in another, the assay was made up to 100 cc. in a graduate and twenty-five cc. were pipetted off and titrated. The former corresponded to 4.48 per cent., the latter to 4.52 per cent. The bulk of the precipitate was approximately one cc., and making the requisite correction gives us 4.48 for the latter result also.

These figures being higher than those obtained directly, I then went back to the use of turmeric, so highly recommended by Pettenkofer, and obtained 4.43 per cent. With great care in the observation of the first brown ring which forms in the presence of the slightest excess of baryta, when a drop of the titrated solution is brought upon turmuric paper, the end reaction can be detected with certainty. The reading is lower than that with phenolphthalein and may be relied upon even with highly colored vinegars. For ordinary purposes, however, the latter indicator with decinormal soda is adequate.

NEW BOOKS.

AN ELEMENTARY COURSE IN EXPERIMENTAL AND ANALYTICAL CHEMISTRY. BY JOHN H. LONG, M.S., Sc.D., PROFESSOR OF CHEMISTRY AND DIRECTOR OF THE CHEMICAL LABORATORIES OF THE SCHOOLS OF MEDICINE AND PHARMACY OF NORTHWESTERN UNIVERSITY. pp. 507. Chicago : E. H. Colegrove & Co.

This book considers three subjects. Part I, covering 275 pages, is devoted to experimental chemistry. The first chapter presents experiments in crystallization, in distillation, and those

that show the difference between physics and chemistry. In the second chapter, oxygen, hydrogen, and their compounds are considered. The halogens and their derivatives constitute the third chapter. At this point elements and compounds, as well as the use of symbols, are discussed. Nitrogen and the atmosphere are the subjects of experimentation in chapter four, while the fifth, sixth, and seventh chapters are occupied by the other frequently occurring non-metals and their derivatives. Seven chapters follow; in them facts relating to the more important metals are presented in simple experiments. Analytical tests follow each metal. Combining weights, the atomic hypothesis, and valency are considered immediately after the metal magnesium. It may be inferred from this that the author advocates first giving to the student an abundance of facts before deducing theories or entering upon a discussion of fundamental principles. This thought is constantly before the reader throughout the entire book. The explanations accompanying the numerous experiments in Part I are clear and to the point. It must be admitted that the author has presented his subject in such a manner that good will result. Part II (twelve chapters) is given to qualitative analysis. The subject-matter is not exhaustive, but here, as in Part I, types are presented to the student. These he works out in detail, being assisted in his efforts by valuable explanatory remarks on the part of the author. Part III considers the elements of volumetric analysis. The examples selected for work are typical and cover a wide field. Recent methods of value have not been overlooked. In this section, as in the two preceding sections, the author has presented all the subject-matter in a very clear style. In short, after careful inspection of the book one lays it down with the conviction that it possesses great merit; it is an excellent book and worthy of commendation.

EDGAR F. SMITH.

ELEMENTS OF MINERALOGY, CRYSTALLOGRAPHY AND BLOWPIPE ANALYSIS. By ALFRED J. MOSES AND CHAS. L. PARSONS. pp. 342, with illustrations. New York: D. Van Nostrand Co., 1895.

This work, as indicated in its preface, is mainly intended for use as a text-book. It is divided into four parts: I. Crystallog-

raphy; II. Blowpipe Analysis; III. Descriptive Mineralogy; IV. Determinative Mineralogy.

The authors have given considerable space to crystallography, having devoted about one-fourth of the entire volume to the subject. The text is well written and fully illustrated.

In part II, after a chapter devoted to the apparatus, flame, etc., there is given a detailed description of the "Operations of Blowpipe Analysis," the reagents employed, and the results obtained in the various manipulations. This is followed by a series of "Useful Tests with the Blowpipe" on all of the principal elements. A valuable feature of this last chapter is a list of "Interfering Elements," which follows tests given for each element and in which directions are given for obtaining the proper reactions. The section is concluded by a chapter on "Schemes for Qualitative Blowpipe Analysis."

Part III, on Descriptive Mineralogy, occupies the major part of the book. The two first chapters treat of the physical characters and chemical composition of minerals. While the definitions of terms are clear and concise, they are in a few cases abridged to incompleteness and explanation of the optical and magnetic properties are omitted entirely.

The remaining chapters describe the various minerals under the heads of the elements forming their principal component parts. A distinguishing and most useful feature of this part of the work are the general remarks at the beginning of each chapter concerning the economic uses of most of the important minerals and ores.

The book would be more useful as one of reference, particularly to the analyst, if more attention had been given to the percentage composition. Many minerals have it in full, others only partially, while not a few have the formula only given.

Part IV consists of a number of tables of the usual tests for the rapid determination of minerals.

The arrangement of the book as a whole is excellent, and although the subject matter has been largely condensed, the elimination of less important details has made it much more practical than text books usually are, and it should be found useful to the professional mineralogist and chemist.

H. B. BALDWIN.